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| (54) Title: OXYGEN SCAVENGERS WITH REDUCED OXIDATION PRODUCTS FOR USE IN PLASTIC FILMS AND BEVERAGE AND FOOD CONTAINERS | | | |
| <div style="text-align: center;"> <p>EMAC</p> <p>3-Cyclohexene-1-methanol</p> <p>Reactive Extrusion (REX)</p> <p>EMCM</p> <p><i>poly(ethylene/methyl acrylate/cyclohexene-methyl acrylate)</i></p> </div> | | | |
| (57) Abstract <p>An oxygen scavenger composition, for use in or with plastics materials, includes a polymer or oligomer having at least one cyclohexene group or functionality. The composition produces only low levels of volatile or (extractable from a plastics material in which it is incorporated) products as a consequence of oxygen scavenging. A family of polymers containing selected cyclic allylic pendent groups for oxygen scavenging packaging which has minimal organoleptic by-products after oxidation. Multilayer plastic containers for food and beverage packaging which incorporate oxygen scavenging resins which selectively oxidize upon activation without giving off odorous fragments.</p> | | | |

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1 OXYGEN SCAVENGERS WITH REDUCED OXIDATION PRODUCTS FOR
2 USE IN PLASTIC FILMS AND BEVERAGE AND FOOD CONTAINERS

3
4
5 Field of the Invention

6 The present invention is directed to oxygen scavengers for use in plastics
7 materials, and in particular plastics films. Emphasis is given to scavengers
8 which produce low or negligible levels of oxidation by-products which may
9 contaminate the head space in a package. This invention also relates to a
10 composition useful in scavenging oxygen from environments containing
11 oxygen-sensitive products, particularly food and beverage products. More
12 specifically, the oxygen scavenging composition includes a polymer having
13 ethylenic unsaturation contained within a cyclic moiety, a transition metal
14 compound and, optionally, a photoinitiator. The present invention also relates
15 to compositions for use in areas such as food packaging, and with minimal
16 effect on odor and taste of packaged contents. The invention preferably uses
17 ethylene acrylate copolymers which are modified with selected cyclic allylic
18 pendent groups for use in oxygen scavenging packaging materials. The
19 present invention also relates to rigid polymeric food or beverage containers
20 comprising polyester such as polyester terephthalate or polyester naphthalate
21 and oxygen scavenging polymer.

22
23
24
25 Background of the Invention

26
27 The majority of plastic films produced are employed in some form of
28 packaging. The present invention is primarily concerned with those films
29 used for applications requiring a low level of oxygen in a package, though
30 may also find other uses.

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1 Limiting the exposure of oxygen-sensitive products to oxygen maintains and
2 enhances the quality and shelf life of many products. For instance, by limiting
3 the oxygen exposure of oxygen-sensitive food products in a packaging
4 system, the quality of the food product can be maintained and spoilage
5 retarded. In addition, such packaging also keeps the product in inventory
6 longer, thereby reducing costs incurred from waste and having to restock.

7
8 In the food packaging industry, several techniques for limiting oxygen
9 exposure have been developed. Common techniques include those where
10 oxygen is consumed within the packaging environment by some means other
11 than the packaged article or the packaging material (e.g., through the use of
12 oxygen scavenging sachets), those where reduced oxygen environments are
13 created in the package (e.g., modified atmosphere packaging (MAP) and
14 vacuum packaging), and those where oxygen is prevented from entering the
15 packaging environment (e.g., barrier films).

16
17 The art dealing with barrier packaging, and the low oxygen or modified
18 packaging of products is relatively well developed. This includes the use of
19 films and inserts containing oxygen scavenging compounds able to extract a
20 majority of any residual oxygen after packaging occurs.

21
22 Oxygen scavenging compounds for use in plastic films are relatively well
23 known. Typically these comprise unsaturated compounds in combination with
24 a transition metal catalyst. In response to some form of initiation—usually
25 exposure to light or radiation—the scavengers react with available oxygen in
26 the package.

27
28 For instance:

29

1 Michael Rooney, "Oxygen scavenging: a novel use of rubber photo-
2 oxidation", *Chemistry and Industry*, March 20, 1982, pp. 197-198, describes
3 the use of ethylenically unsaturated compounds as oxygen scavengers on
4 exposure to light. However, systems describing the use of transition metal
5 catalysts are not described.

6

7 US 4,908,151 to Mitsubishi describes sachets containing unsaturated fatty
8 acid (i.e., an ethylenically unsaturated hydrocarbon) in combination with a
9 transition metal compound in a basic substance. However, there is no
10 description of these materials in the form of a film nor the use of photo-
11 exposure as an initiating mechanism.

12

13 Japanese patent JP5032277 to Kuwa describes the use of radical containing
14 resin layers in packages. The invention comprises an oxidizable polymer
15 whose oxygen scavenging abilities is photoinitiated.

16

17 New Zealand patent application NZ241802 to W R Grace and also NZ243077
18 also to W R Grace, claim oxygen scavenging compositions comprising
19 ethylenically unsaturated hydrocarbons with transition metal catalysts. A wide
20 range of ethylenically unsaturated compounds are discussed in the texts of
21 these specifications though there is no mention of the problems to which the
22 present invention is directed, nor the compounds and products encompassed
23 by the present invention.

24

25 Sachets containing an oxygen scavenging compositions can contain ferrous
26 compositions, which oxidize to their ferric state, unsaturated fatty acid salts on
27 an absorbent, and/or a metal-polyamide complex. See, e.g., U.S. Patent
28 Nos. 4,908,151 and 5,194,478. The disadvantages of sachets include the
29 need for additional packaging steps (to add the sachet to the package), the

1 potential for contamination of the packaged article should the sachet break
2 and the danger of ingestion by a consumer.

3

4 Oxygen scavenging materials also have been incorporated directly into the
5 packaging structure. This technique (hereinafter referred to as "active oxygen
6 barrier") can provide a uniform scavenging effect throughout the package and
7 can provide a means of intercepting and scavenging oxygen as it passes
8 through the walls of a package, thereby maintaining the lowest possible
9 oxygen level throughout the package. Active oxygen barriers have been
10 formed by incorporating inorganic powders and/or salts as part of the
11 package. See, e.g., U.S. Patent Nos. 5,153,038, 5,116,660, 5,143,769, and
12 5,089,323. However, incorporation of such powders and/or salts can degrade
13 the transparency and mechanical properties (e.g., tear strength) of the
14 packaging material and can complicate processing, especially where thin
15 films are desired. Also, these compounds as well as their oxidation products
16 can be absorbed by food in the container, which can result in the food product
17 failing to meet governmental standards for human consumption.

18

19 EP 0 519 616 discloses an oxygen scavenging composition that includes a
20 blend of an epoxide, a first polymeric component grafted with an unsaturated
21 carboxylic anhydride and/or acid, a second polymeric component including
22 OH, SH, or NHR^2 groups where R^2 is H, $\text{C}_1\text{-C}_3$ alkyl, or substituted $\text{C}_1\text{-C}_3$ alkyl
23 moiety, and a metal salt capable of catalyzing the reaction between oxygen
24 and the second polymeric component. The first polymeric component is
25 present in an amount sufficient to ensure that the blend is non-phase
26 separated. A blend of polymers is utilized to obtain oxygen scavenging, and
27 the second polymeric component is preferably a (co)polyamide such as
28 MXD6.

29

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1 Another type of active oxygen barrier is illustrated in EP-A-0 301 719,
2 EP-A-0 380 319, PCT Publication No. WO 90/00578, and PCT Publication
3 No. WO 90/00504. See also U.S. Patent Nos. 5,021,515 5,194,478, and
4 5,159,005. The disclosed oxygen scavenger includes polyamide-transition
5 metal catalyst compositions. Through catalyzed scavenging by the
6 polyamide, the package wall regulates the amount of oxygen reaching the
7 interior of the package. However, the onset of useful oxygen scavenging (i.e.,
8 up to about $5.8 \times 10^{-5} \text{ cm}^3/\text{m}^2 \cdot 24 \text{ hours}$ at ambient conditions) can take as
9 long as 30 days to occur. Therefore, this technique is not acceptable for
10 many applications. Further, polyamides typically are incompatible with many
11 thermoplastic polymers commonly used to make flexible packaging materials
12 (e.g., ethylene/vinyl acetate copolymers, low density polyethylene, etc.) or,
13 when used by themselves, are difficult to process and result in inappropriately
14 stiff structures.

15

16 Oxygen scavenging compositions that include transition metal catalysts and
17 ethylenically unsaturated hydrocarbon polymers which have an ethylenic
18 double bond content of from 0.01 to 10 equivalents per 100 grams of polymer
19 are disclosed in U.S. Patent No. 5,399,289. Various conventional
20 homopolymers, copolymers, and polymer blends are disclosed. Because
21 these polymers are amorphous, they can be difficult to blend and process
22 with film-forming semicrystalline polymers conventionally used to make
23 flexible packaging materials.

24

25 The use of a transition metal and a photoinitiator to facilitate initiation of
26 effective scavenging activity of ethylenically unsaturated compounds is taught
27 in U.S. Patent No. 5,211, 875, which is incorporated herein by reference as if
28 set forth in full.

29

1 PCT Publication Nos. WO 95/02616 and WO 96/40799 disclose a scavenger
2 composition that includes a transition metal salt and a copolymer (of ethylene
3 and a vinyl monomer) having ether, amino, carboxylic acid, ester, or amide
4 functionalities pendent therefrom. Although these compositions can provide
5 oxygen scavenging activity, the particular advantages of having ethylenic
6 unsaturation contained within a cyclic moiety are not disclosed. Because the
7 compositions of this invention are significantly cleaner than those described in
8 the prior art, they do not require the use of high levels of adjuncts to absorb
9 the undesirable byproducts. Such absorbent additives are known in the art,
10 for example see U.S. 5,834,079 and U.S. 08/857,276. It is also well known in
11 the art that such additives (zeolites and silicas) adversely affect the haze and
12 clarity of packaging structures.

13
14 PCT Application WO 96/40799 from Chevron describes the use of a variety of
15 ethylenic materials with benzylic, allylic or ether containing side chains. Some
16 of these materials may be prepared by esterification or transesterification of a
17 polymer melt. The use of pendent cyclic groups containing allylic
18 unsaturation is generally referred to, but there is only one such example,
19 wherein Nopol, a bicyclic alcohol, is used in a transesterification reaction and
20 oxygen absorbing films are formulated from the product. There is no
21 reference to the benefits of cyclic allylic compounds as described in this
22 invention i.e., on oxidation they produce very low levels of oxidation
23 byproducts when compared to comparable linear allylic systems. Because of
24 its bicyclic nature, Nopol is not expected to produce these benefits.

25
26 While the prior art compounds may effectively scavenge oxygen they
27 introduce other problems into packaging. For instance, in summary the prior
28 art incorporates into film structures compounds which are ethylenically
29 unsaturated but which often cleave as a consequence of the reactions of the
30 oxygen scavenging process. For example, films containing unsaturated

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1 compounds such as squalene or vegetable oils produce large amounts of
2 volatile aldehydes and ketones upon oxidation. Unfortunately, many of these
3 volatile compounds are not contained within the film structure and find their
4 way into the head space of the package. Here they can represent more of a
5 problem than the oxygen which they have replaced and have the potential to
6 contaminate comestible products.

7

8 This problem represents a significant problem yet has been downplayed or
9 overlooked by the published prior art. As a consequence, those searching
10 the prior art for a solution to this problem find no answer—the art appears to
11 be directed primarily along a narrow track of improving on scavenging
12 efficiencies, or physical properties of scavenging films, rather than
13 recognizing or addressing other associated problems.

14

15 Accordingly the present invention seeks to address the problems associated
16 with scission products of oxygen scavengers, and seeks also to provide a
17 group of compounds and substances (as well as films and plastics materials
18 including same) which have an advantage over the prior art in terms of
19 reduced quantities of scission products.

20

21 Ideally, a polymeric material for use in an oxygen scavenging composition
22 should exhibit good processing characteristics, be able to be formed into
23 useful packaging materials or have high compatibility with those polymers
24 commonly used to make packaging materials, and not produce byproducts
25 which detract from the color, taste, or odor of the packaged product. It has
26 been found that when the ethylenic unsaturation is contained within a cyclic
27 group, substantially fewer and less byproducts are produced upon oxidation
28 as compared to analogous non-cyclic materials. Optimally, a packaging

1 material formed from such a composition can retain its physical properties
2 after significant oxygen scavenging.

3

4

5 New polymer compositions having properties that are particularly tailored for
6 specific applications are required in response to more specific and
7 sophisticated end uses. It can be difficult to make these compositions directly
8 by polymerization from monomers or via solution esterification or
9 transesterification, but manufacturing them in melt mixing equipment such as
10 an extruder has provided an efficient, economical and viable means to supply
11 increasingly complex polymers to meet the needs in specialized markets.

12 It is well known that regulating the exposure of oxygen-sensitive products to
13 oxygen maintains and enhances the quality and "shelf-life" of the product.
14 For instance, by limiting the exposure of oxygen sensitive food products to
15 oxygen in a packaging system, the quality or freshness of food is maintained,
16 spoilage reduced and the food shelf life extended. In the food packaging
17 industry, several means for regulating oxygen exposure have already been
18 developed. These means include modified atmosphere packaging (MAP) and
19 oxygen barrier film packaging.

20 One method currently being used is "active packaging", whereby the package
21 containing the food product has been modified in some manner to regulate
22 the food's exposure to oxygen. One form of active packaging uses oxygen-
23 scavenging sachets which contain a composition which scavenges the
24 oxygen through oxidation reactions. One type of sachet contains iron-based
25 compositions which oxidize to their ferric states. Another type of sachet
26 contains unsaturated fatty acid salts on a particulate adsorbent. Yet another
27 sachet contains metal/polyamide complex. However, one disadvantage of

1 sachets is the need for additional packaging operations to add the sachet to
2 each package. A further disadvantage arising from the iron-based sachets is
3 that certain atmospheric conditions (e.g., high humidity, low CO₂ level) in the
4 package are sometimes required in order for scavenging to occur at an
5 adequate rate. Further, the sachets can present a problem to consumers if
6 accidentally ingested.

7 Another means for regulating exposure of a packaged product to oxygen
8 involves incorporating an oxygen scavenger into the packaging structure
9 itself. A more uniform scavenging effect through the package is achieved by
10 incorporating the scavenging material in the package instead of adding a
11 separate scavenger structure (e.g., a sachet) to the package. This may be
12 especially important where there is restricted airflow inside the package. In
13 addition, incorporating the oxygen scavenger into the package structure
14 provides a means of intercepting and scavenging oxygen as it permeates the
15 walls of the package (herein referred to as an "active oxygen barrier"),
16 thereby maintaining the lowest possible oxygen level in the package.

17 One attempt to prepare an oxygen-scavenging wall involves the incorporation
18 of inorganic powders and/or salts. However, incorporation of these powders
19 and/or salts causes reduction of the wall's optical transparency, discoloration
20 after oxidation, and reduced mechanical properties such as tear strength. In
21 addition, these compounds can lead to processing difficulties, especially
22 when fabricating thin films. The oxidation products may migrate into food at
23 levels which would not be regarded as safe or can impart unacceptable taste
24 or smell to food.

25 An oxygen-scavenging composition comprising a blend of a first polymeric
26 component comprising a polyolefin is known, the first polymeric component
27 having been grafted with an unsaturated carboxylic anhydride or an
28 unsaturated carboxylic acid, or combinations thereof, or with an epoxide; a

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1 second polymeric component having -OH, -SH, or -NHR² groups where R² is
2 H, C₁-C₃ alkyl, substituted C₁-C₃ alkyl; and a catalytical amount of metal salt
3 capable of catalyzing the reaction between oxygen and the second polymeric
4 component, the polyolefin being present in an amount sufficient so that the
5 blend is not phase-separated. A blend of polymers is utilized to obtain
6 oxygen scavenging, and the second polymeric component is preferably a
7 polyamide or a copolyamide such as the copolymer of m-xylylene-diamine
8 and adipic acid (MXD6).

9 Some oxygen scavenging systems produce an oxygen-scavenging wall. This
10 is done by incorporating a metal catalyst-polyamide oxygen scavenging
11 system into the package wall. Through catalyzed oxidation of the polyamide,
12 the package wall regulates the amount of oxygen which reaches the interior
13 volume of the package (active oxygen barrier) and has been reported to have
14 oxygen scavenging rate capabilities up to about 5 cubic centimeters (cc)
15 oxygen per square meter per day at ambient conditions. However, this
16 system suffers from significant disadvantages.

17 One particularly limiting disadvantage of polyamide/catalyst materials can be
18 a low oxygen scavenging rate. Adding these materials to a high-barrier
19 package containing air can produce a package which is not generally suitable
20 for creating an internal oxygen level of less than 0.1% within seven days at
21 storage temperatures, as is typically required for headspace oxygen
22 scavenging applications.

23 There are also disadvantages to having the oxygen-scavenging groups in the
24 backbone or network structure in this type of polyamide polymer. The basic
25 polymer structure can be degraded and weakened upon reaction with oxygen.
26 This can adversely affect physical properties such as tensile or impact
27 strength of the polymer. The degradation of the backbone or network of the

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1 polymer can further increase the permeability of the polymer to those
2 materials sought to be excluded, such as oxygen.

3 Moreover, polyamides previously used in oxygen scavenging materials, such
4 as MXD6, are typically incompatible with thermoplastic polymers used in most
5 flexible packaging walls, such as ethylene-vinyl acetate copolymers and low
6 density polyethylene. Even further, when such polyamides are used by
7 themselves to make a flexible package wall, they may result in inappropriately
8 stiff structures. They also incur processing difficulties and higher costs when
9 compared with the costs of thermoplastic polymers typically used to make
10 flexible packaging. Even further, they are difficult to heat seal. Thus, all of
11 these are factors to consider when selecting materials for packages,
12 especially multi-layer flexible packages and when selecting systems for
13 reducing oxygen exposure of packaged products.

14 Another approach to scavenging oxygen is an oxygen-scavenging
15 composition comprising an ethylenically unsaturated hydrocarbon and a
16 transition metal catalyst. Ethylenically unsaturated compounds such as
17 squalene, dehydrated castor oil, and 1,2-polybutadiene are useful oxygen
18 scavenging compositions, and ethylenically saturated compounds such as
19 polyethylene and ethylene copolymers are used as diluents. Compositions
20 utilizing squalene, castor oil, or other such unsaturated hydrocarbon typically
21 have an oily texture as the compound migrates toward the surface of the
22 material. Further, polymer chains which are ethylenically unsaturated in the
23 backbone would be expected to degrade upon scavenging oxygen,
24 weakening the polymer due to polymer backbone breakage, and generating a
25 variety of off-odor/off-taste by-products.

26 Other oxidizable polymers recognized in the art include "highly active"
27 oxidizable polymers such as poly(ethylene-methyl acrylate-benzyl acrylate),
28 EMBZ, and poly(ethylene-methyl acrylate-tetrahydrofurfuryl acrylate), EMTF,

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1 as well as poly(ethylene-methyl acrylate-nopol acrylate), EMNP. Although
2 effective as oxygen scavengers, these polymers have the drawback of giving
3 off large amounts of volatile by-products and/or strong odors after oxygen
4 scavenging.

5 Also known are oxygen-scavenging compositions which comprise a transition-
6 metal salt and a compound having an ethylenic backbone and having allylic
7 pendent or terminal moieties which contain a carbon atom that can form a
8 free radical that is resonance-stabilized by an adjacent group. Such a
9 polymer needs to contain a sufficient amount and type of transition metal salt
10 to promote oxygen scavenging by the polymer when the polymer is exposed
11 to an oxygen-containing fluid such as air. Although effective as oxygen
12 scavengers, upon oxidation, we have found that allylic pendent groups on an
13 ethylenic backbone tend to generate considerable amounts of organic
14 fragments. We believe this is a result of oxidative cleavage. We believe
15 these fragments can interfere with the use of allylic pendent groups as
16 oxygen scavengers in food packaging.

17 Multilayer rigid container structures, which utilize an oxygen scavenging
18 composition, are known. In the container wall, base polymers such as
19 polyethylene terephthalate have been used along with an oxygen scavenger.
20 The resulting multilayer package wall includes at least an oxygen scavenger
21 core layer as well as inner and outer layers having high oxygen barrier
22 qualities. The oxygen scavenger core layer is a combination of at least an
23 oxygen scavenging polymer with post consumer-polyethylene terephthalate
24 (PC-PET). The inner and outer layers include at least oxygen barrier quality
25 PET.

26

27 Furthermore, multilayered plastic bottles having oxygen scavenging capacity
28 sufficient to maintain substantially zero or near zero presence of oxygen in

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1 the bottle cavity under specified storage conditions have also been disclosed.
2 The multilayered bottle wall has at least three layers. The inner and outer
3 layers are PET or another bottling polyester, which define the bottle cavity
4 and the outside skin of the bottle respectively. Between the inner and outer
5 layers is an oxygen scavenging copolyester layer.

6
7 Condensation copolymers used for making bottles with polyester such as
8 PET or polyethylene naphthalate (PEN) have also been disclosed. The
9 condensation copolymers comprise predominantly polyester segments and
10 an oxygen scavenging amount of polyolefin oligomer segments. The
11 copolymers are preferably formed by transesterification during reactive
12 extrusion and typically comprise about 0.5 to about 12 wt. % of polyolefin
13 oligomer segments. In a preferred embodiment, a bottle is provided having a
14 multilayer wall of at least three layers. The outer and inner layers are of
15 unmodified PET and the oxygen scavenging layer in between the outer and
16 inner layer is made of the condensation copolymers described above having
17 an oxygen scavenging amount of polyolefin oligomers.

18
19 A transparent oxygen-scavenging article for packaging oxygen sensitive
20 products is also known, the oxygen-scavenging article having a multilayered
21 wall including at least three layers, an inner and outer layer of biaxially-
22 oriented aromatic polyester polymers such as PET or PEN and an oxygen-
23 scavenging aromatic ester polymer compatible with the polyester polymer.
24 The oxygen-scavenging aromatic ester polymer must include ketone carbonyl
25 groups to provide the oxygen-scavenging functionality and aromatic and ester
26 groups for compatibility with the polyester.

27
28 PET containers have been disclosed that have a container wall of stretched
29 plastic material with high oxygen barrier properties and an activating metal
30 incorporated into the plastic material. The plastic material is PET in admixture

1 with a polyamide and the metal is either added to the mixture or contained in
2 one or both of the polymers.

3

4 A container containing at least one layer containing a plastics material and
5 ions of at least one metal has also been disclosed. The plastics material in
6 the layer consists of at least a partially split or degraded polyamide which has
7 increased sensitivity to reaction with oxygen in the presence of metal thus
8 giving the layer improved oxygen barrier properties.

9

10 A container has been disclosed with a wall having high oxygen barrier
11 properties comprising a molded polymer composition, the composition
12 comprising a granular mixture of (1) a first polymer providing essential
13 strength for the container wall and (2) an active component comprising a
14 metal compound capable of scavenging oxygen and consisting essentially of
15 a metal ion having complexing properties and a polymer to which said metal
16 ion is combined as a metal complex in the molded polymer composition of
17 said wall to scavenge oxygen. There is also disclosed a method of producing
18 the polymer composition which can be molded into containers, the method
19 being to treat a polymer with a metal compound dissolved or slurried in a
20 volatile solvent composition during refluxing conditions for obtaining the active
21 component having capacity to scavenge oxygen.

22

23 An article has been disclosed with oxygen barrier properties comprising at
24 least partly a molded polymer composition formed by melting granules of the
25 composition and molding the melted composition to produce the article. The
26 composition comprises a granular mixture of (1) a first polymer composition
27 providing strength for the article and (2) a second polymer composition
28 compatible with the first polymer composition. The second polymer
29 composition is obtainable by reacting a polyamide or copolyamide with a
30 solution of a transition metal compound in a volatile solvent under refluxing

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1 conditions. The polymer of the first polymer composition can be any polymer
2 and the metal of the metal compound reacted with the polyamide or
3 copolyamide can be any transition metal. The amount of metal in the second
4 polymer composition is at least 500 ppm.

5
6 A polymer material having increased sensitivity to reaction with oxygen has
7 also been disclosed, the polymer material comprising a polyamide, which has
8 been reacted with a nucleophilic reagent and possibly an activator. The
9 nucleophilic reagent is selected from the group consisting of compounds
10 containing at least one hydroxyl group, compounds containing at least one
11 alkoxide group, phosphate compounds, pyrophosphate compounds,
12 polyphosphate compounds, salts of organic acids and a copolymer of vinyl
13 alcohol and ethylene. The activator is in the form of a hydrogen donor. A
14 process is also disclosed for producing the polymer material, which has
15 increased sensitivity of reaction with oxygen. In the process, a polyamide
16 reacts with the nucleophilic reagent under such conditions that the polymer
17 material is obtained.

18
19 Such polymeric containers of PET, PEN and/or polyamide as described
20 above utilize oxidizable components to react with and decrease the amount of
21 oxygen in contact with oxygen sensitive materials packaged in containers. All
22 of these oxidizable materials have the disadvantage of imparting unpleasant
23 odor and/or taste to the packaged materials because of the byproducts given
24 off during the oxidation of the oxidizable materials. Another problem is the
25 uncontrolled oxidation fragmentation from the polymer backbone which leads
26 to chain secession, thus weakening the physical integrity of the multilayer
27 container structures.

28

29

-16-

1 The present invention solves many of the problems of the prior art, especially
2 with an oxygen scavenging packaging material incorporating polymers
3 comprising cyclic allylic (olefinic) pendent groups which produce little or no
4 migration of oxidation by-products adversely affecting odor or taste, thus
5 minimizing organoleptic problems in food packaging. This is because the
6 cyclic allylic structures are less likely to fragment or cleave after oxidation
7 than the conventional open chain allylic (olefinic) groups used in oxygen
8 scavenging packaging material.

9
10 Such polymeric containers of PET, PEN and/or polyamide as described
11 above utilize oxidizable components to react with and decrease the amount of
12 oxygen in contact with oxygen sensitive materials packaged in containers. All
13 of these oxidizable materials have the disadvantage of imparting unpleasant
14 odor and/or taste to the packaged materials because of the byproducts given
15 off during the oxidation of the oxidizable materials. Another problem is the
16 uncontrolled oxidation fragmentation from the polymer backbone which leads
17 to chain secession, thus weakening the physical integrity of the multilayer
18 container structures.

19
20 In contrast, the present invention achieves a rigid beverage and food
21 container comprising PET and/or PEN, the container incorporating an oxygen
22 scavenging component of cyclic olefin which does not give off odor and or
23 taste as a result of its oxygen scavenging function. The oxidation also does
24 not cause a change in molecular weight. This is because the cyclic olefin
25 oxygen scavenging component does not fragment as it oxidizes, thus
26 avoiding the problem of imparting oxidation byproducts to the packaged
27 material while maintaining the structural integrity.
28

1 It is an object of the present invention to address the foregoing problems or at
2 least to provide the public with a useful choice.

3

4 Further aspects and advantages of the present invention will become
5 apparent from the ensuing description, which is given by way of example
6 only.

7

8 SUMMARY OF INVENTION

9

10 According to one aspect of the present invention, there is provided an oxygen
11 scavenger for use in or with plastics materials, said scavenger comprising or
12 including a polymer or oligomer having at least one cyclohexene group or
13 functionality.

14

15 According to another aspect of the present invention, there is provided an
16 oxygen scavenger, substantially as described above, which produces only
17 low levels of volatile or extractable (from a plastics material in which it is
18 incorporated) products as a consequence of oxygen scavenging.

19

20 According to another aspect of the present invention there is provided an
21 oxygen scavenger, substantially as described above, which is substantially
22 stable with respect to reaction with oxygen until triggered by an external
23 event.

24

25 According to another aspect of the present invention, there is provided an
26 oxygen scavenger, substantially as described above, wherein the external
27 event is irradiation by electromagnetic radiation.

28

29 According to a further aspect of the present invention, there is provided an
30 oxygen scavenging composition, including an oxygen scavenger,

1 substantially as described above, which includes one or more trigger
2 enhancing components making the scavenger susceptible to triggering from
3 an external event.

4

5 According to another aspect of the present invention, there is provided an
6 oxygen scavenging composition, substantially as described above, wherein a
7 trigger-enhancing component may be benzophenone or substituted
8 derivatives thereof.

9

10 According to another aspect of the present invention, there is provided an
11 oxygen scavenging composition, substantially as described above, which
12 includes the presence of one or more catalysts for the scavenging process.

13

14 According to another aspect of the present invention, there is provided an
15 oxygen scavenging composition, substantially as described above, in which a
16 catalyst may be a transition metal salt, compound or complex.

17

18 According to another aspect of the present invention, there is provided an
19 oxygen scavenger or oxygen scavenging composition, substantially as
20 described above, which is in the form of a plastics resin.

21

22 According to another aspect of the present invention, there is provided an
23 oxygen scavenger or oxygen scavenging composition, substantially as
24 described above, in which the plastics resin is a resin suitable for use in the
25 manufacture of plastic films.

26

27 According to another aspect of the present invention, there is provided an
28 oxygen scavenger or oxygen scavenging composition, substantially as
29 described above, in which the plastic resin is a polyester resin.

30

1 According to another aspect of the present invention, there is provided an
2 oxygen scavenger or oxygen scavenging composition, substantially as
3 described above, when present in a plastics film or layer thereof.

4

5 According to another aspect of the present invention, there is provided an
6 oxygen scavenger or oxygen scavenging composition, substantially as
7 described above, when used as a polymeric material of a plastics film, a layer
8 thereof, and/or a coating thereof, or in a plastics material.

9

10 According to another aspect of the present invention, there is provided an
11 oxygen scavenger or oxygen scavenging composition, substantially as
12 described above, when dispersed throughout a plastics film, a layer thereof,
13 and/or a coating thereon, or in a plastics material.

14

15 According to a further aspect of the present invention, there is provided an
16 oxygen scavenger or oxygen scavenging composition, substantially as
17 described above, in which the anhydride comprises 1,2,3,6-tetrahydrophthalic
18 anhydride or tetrahydrophthalic anhydride monomer derivable from
19 butadiene.

20

21 According to a further aspect of the present invention, there is provided an
22 oxygen scavenger or oxygen scavenging composition prepared from the
23 reaction of a tetrahydrobenzyl alcohol with one or more compounds having
24 one or more of the following functionalities: carboxylic acid, acid halide, ester,
25 anhydride, and isocyanate.

26

27 According to another aspect of the present invention, there is provided an
28 oxygen scavenger or oxygen scavenging composition, substantially as
29 described above, in which the alcohol comprises tetrahydrobenzyl alcohol.

30

1 According to another aspect of the present invention, there is provided an
2 oxygen scavenger or oxygen scavenging composition, substantially as
3 described above, in the compounds with which the alcohol is reacted may
4 include a styrene maleic anhydride copolymer, and/or a polyfunctional
5 isocyanate.

6

7 According to another aspect of the present invention, there is provided an
8 oxygen scavenger or oxygen scavenging composition, prepared from a
9 cyclohexene dimethanol compound.

10

11 According to another aspect of the present invention, there is provided an
12 oxygen scavenging polymer including at least one pendant cyclohexene
13 group prepared by a reactive extrusion process.

14

15 According to a further aspect of the present invention, there is provided an
16 oxygen scavenger or oxygen scavenging polymer, substantially as described
17 above, in which the reactive extrusion process comprises an esterification or
18 transesterification step. Suitable catalyst include acids, bases and
19 organometallic compounds such as the titanium alkoxides.

20

21 According to another aspect of the present invention, there is provided an
22 oxygen scavenger or oxygen scavenging polymer prepared by a route
23 including a cyclohexene anhydride.

24

25 According to another aspect of the present invention, there is provided an
26 oxygen scavenger or oxygen scavenging polymer prepared by a route
27 including the reaction of a diene monomer, or hydroxy containing monomer,
28 with a cyclic anhydride.

29

1 According to another aspect of the present invention, there is provided an
2 oxygen scavenger or oxygen scavenging polymer, substantially as described
3 above, in which the cyclic anhydride is a maleic anhydride.

4

5 According to a further aspect of the present invention, there is provided an
6 oxygen scavenger including a pendant cyclic alkene group prepared via a
7 method including a Diels Alder addition reaction.

8

9 According to another aspect of the present invention, there is provided an
10 oxygen scavenger, substantially as described above, in which the preferred
11 dienes for use in the Diels Alder reaction is substituted and/or unsubstituted
12 1,3 butadiene.

13 According to another aspect of the present invention, there is provided an
14 oxygen scavenger, substantially as described above, in which the preferred
15 dienophile for use in the Diels Alder reaction include unsaturated acids,
16 anhydrides, and esters.

17

18 According to another aspect of the present invention, there is provided an
19 oxygen scavenger, substantially as described above, in which the cyclic
20 alkene is cyclohexene.

21

22 In other aspects, the present invention provides an article which include at
23 least one layer formed from a blend that includes the foregoing composition
24 as well as a method of scavenging oxygen in which a packaging article, at
25 least one layer of which is formed from a blend that includes the foregoing
26 composition, is exposed to actinic or e-beam radiation so as to activate the
27 composition.

28

-22-

1 According to a further aspect of the present invention, there is provided an
2 oxygen scavenger or oxygen scavenging composition prepared from a
3 tetrahydrophthalic anhydride and a polymer or lower molecular weight
4 compound containing at least one amine group.

5

6 According to a further aspect of the present invention, there is provided an
7 oxygen scavenger or oxygen scavenging composition prepared from
8 diglycidyltetrahydrophthalate.

9 According to a further aspect of the present invention, there is provided an
10 oxygen scavenger or oxygen scavenging composition prepared from the
11 reaction of tetrahydrobenzyl alcohol, methyl or dimethyl substituted
12 tetrahydrobenzyl alcohol with one or more compounds having one or more of
13 the following functionalities: carboxylic acid, acid halide, ester, anhydride,
14 epoxide and isocyanate.

15

16 According to a further aspect of the present invention, there is provided an
17 oxygen scavenger or oxygen scavenging composition, substantially as
18 described above, in which a tetrahydrobenzyl alcohol or substituted
19 tetrahydrobenzyl alcohol reacts with one or more of the following materials:

20

21 ethylene (meth)acrylic acid and other acid containing polymers and acid
22 containing lower molecular weight materials;

23

24 styrene maleic anhydride copolymers; alpha olefin maleic anhydride
25 copolymers such as octadecene maleic anhydride; ethylene and ethylene
26 alpha olefin maleic anhydride terpolymers; ethylene alkyl (meth) acrylate
27 maleic anhydride terpolymers and other like anhydride containing polymers or
28 anhydride containing lower molecular weight materials;

29

-23-

1 polymeric or lower molecular weight materials containing acid halide
2 functionality such as poly acryloyl chloride;
3
4 ethylene alkyl (meth)acrylate copolymers and terpolymers and alternative
5 polymers or lower molecular weight materials containing lower alkyl ester
6 functionality;

7

8 epoxy resins;

9

10 isocyanate functional material such as prepolymers and oligomers derived
11 from the common diisocyanates such as MDI, TDI and the like.

12

13 According to a further aspect of the present invention, there is provided an
14 oxygen scavenger or oxygen scavenging composition prepared from a
15 dihydroxy cyclohexene compound. For example, 3 Cyclohexene-1,1-
16 dimethanol or its substituted derivatives may be used to prepare polyurethane
17 and polyester resins.

18

19 According to a further aspect of the present invention, there is provided an
20 oxygen scavenger or oxygen absorbing composition prepared from a
21 cyclohexene carboxylic acid. Such materials may be prepared from acrylic
22 acid and substituted and unsubstituted butadienes. A typical example would
23 be tetrahydrobenzoic acid, derived from acrylic acid and butadiene. This may
24 be reacted with the following materials:

25

26 hydroxyl functional materials such as poly(vinyl alcohol) and polyethylene-
27 vinyl alcohol, hydroxyl functional oligomers such as poly(ethylene glycol), the
28 polyester polyols and other lower molecular weight hydroxyl functional
29 materials;

30

1 amine functional polymers and lower molecular weight compounds;

2

3 polyvalent metal ions.

4

5 According to a further aspect of the present invention, there is provided an

6 oxygen scavenger prepared from a cyclohexene functional acid chloride.

7 Example 9 utilizes 3-cyclohexene-1-carbonyl chloride.

8

9 According to a further aspect of the present invention, there is provided an

10 oxygen scavenger or oxygen scavenging composition prepared from

11 tetrahydrobenzaldehyde and its substituted derivatives. These may be

12 prepared from reaction of butadiene or the methyl substituted butadienes with

13 acrolein.

14

15 The tetrahydrobenzaldehydes may be reacted with hydroxyl functional

16 polymers such as poly(vinyl alcohol) and polyethylene-vinyl alcohol to form

17 polyvinyl acetals.

18

19 The following definitions apply herein throughout unless a contrary intention is

20 expressly indicated:

21

22 "polymer" means the polymerization product of one or more monomers and

23 includes homopolymers, as well as copolymers;

24 "copolymer" means the polymerization product of two or more kinds of

25 monomers;

26

27 "(meth)acrylate" means acrylate or methacrylate;

28

29 "photoinitiator" means a substance which, when activated by actinic radiation,

30 enhances and/or facilitates the initiation of one or more properties (e.g.,

1 oxygen scavenging) in another compound, thus resulting in a shorter
2 induction period and/or an increase in the rate of oxygen uptake of the overall
3 system;

4

5 "induction period" means the length of time beginning with the initiation of the
6 active components of a composition and ending with the onset of one or more
7 useful properties (e.g., oxygen scavenging); and

8

9 "antioxidant" means a material which can inhibit oxidative degradation and/or
10 crosslinking of a poly polymer so as to, for example, prolong the useful
11 lifetime of the polymer, to stabilize a polymer-containing composition during
12 processing (e.g., extrusion, coating, lamination, etc.); and/or to prolong the
13 shelf-life of the composition (prior to exposure thereof to actinic or e-beam
14 radiation).

15

16 The present invention is directed to oxygen scavengers. The invention
17 includes oxygen scavenging substances, as well as compositions containing
18 same. The form of the oxygen scavengers may vary and may comprise small
19 molecules through to large macromolecules as well as those sized in
20 between. The oxygen scavengers will be characterized in that they will be
21 able to react with oxygen in their near vicinity, enabling the removal of oxygen
22 from a closed system.

23

24 While the actual form of the oxygen scavengers may vary, a characteristic
25 that they each share is they include cyclic alkene groups or functionalities,
26 which are able to react with oxygen to provide the desired oxygen scavenging
27 properties. In preferred embodiments of the present invention, this will
28 comprise a cyclohexene group i.e. a six-membered ring with double bond
29 between two adjacent carbon atoms. It is acceptable that some carbons of

1 the cyclohexene group may also form a part of other ring structures within the
2 molecule, and/or form part of the skeleton of the molecule. It is not necessary
3 that the entire C₆ ring be dangling free of the remainder of the molecule to
4 which it is attached. A consideration however is that the group should be so
5 positioned and incorporated into the structure that the double bond is
6 available for reaction with oxygen.

7

8 It has been mentioned above that various scavengers of the present invention
9 may take different forms. This will also have some bearing on how they are
10 used, and also produced. Perhaps the simplest embodiments of the present
11 invention are short molecules containing a reactive cyclohexene group, which
12 may be dispersed in an appropriate medium for use. This may include the
13 use of short molecules (see also later) which can be dispersed within a
14 plastics resin or material. The ultimate result would be a plastics film or
15 material incorporating the oxygen scavenger. Of course, consideration would
16 need to be given to accessibility of the scavengers of the oxygen being
17 scavenged though this may rely on the porosity of the film (or film
18 layer/material) in which it is incorporated, or alternatively may be presented in
19 the manner of a coating with a reactive surface.

20

21 While the use of oxygen scavengers of varying sizes, (though typically those
22 of smaller size), dispersed through plastics materials is envisaged, oxygen
23 scavengers according to the present invention may also be used in other
24 ways.

25

26 For instance, they may be dispersed throughout non-plastics materials. This
27 may include inert and inorganic materials. This may also include other
28 liquids. It is envisaged that such embodiments of the present invention may
29 be used in applications such as sachets inserted into closed packages. The

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1 use of oxygen scavengers in sachets and package inserts is documented in
2 the art and the same principles may be applied here.

3

4 Another means by which the present invention may be applied is through the
5 use of plastics resins incorporating the desired scavenging functionalities.
6 These resins, which for instance may include polyester resins, may be used
7 in the various manners by which resins are normally used. This may include
8 film production, resin coatings, as well as molding or extrusion techniques.

9 Another method by which the present invention may be implemented is the
10 formation or modification of polymers to contain the desired scavenging
11 functionalities and groups. In such cases, the film or plastics material itself
12 will possess oxygen scavenging properties. It is envisaged that such
13 materials may exist as layers in multi-layer films. Such polymers may also be
14 introduced as copolymers or blends in film and plastics manufacturing
15 methods.

16

17 The above instances of how embodiments of the present invention may be
18 used are illustrative only. It is noted that the use of oxygen scavenging
19 materials is known in the art, and that art may be drawn upon to further
20 expand the illustrative examples given within this specification.

21

22 Embodiments of the present invention based on cyclohexene groups appear
23 to afford significant advantage over the prior art. This advantage is in the
24 number and nature of the oxidation product once the scavenging is
25 completed. In the prior art, heavily reliance is made on straight chain
26 alkenes, such as for instance fatty acids. The problem however, is that film
27 containing unsaturated compounds such as squalene or vegetable oils
28 produce large amounts of volatile aldehydes and ketones upon oxidation.
29 These tend to be released, or leach, from the plastics material over time,

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1 usually find their way into the head space of the packaged material. The
2 presence of these foreign substances can represent a significant problem,
3 which the use of cyclohexene scavenging groups addresses at least partially.
4

5 In comparison, there are significantly less scission products from oxidation
6 reactions involving cyclohexene groups—the oxidation of the cyclohexene
7 group does not normally involve ring breakage. If the remainder of the
8 molecule to which the cyclohexene group is attached is bound or linked to the
9 polymeric structure of the material in which it is incorporated or affixed, or
10 otherwise bound or held in place to the material through which it is dispersed
11 or incorporated, then there is little chance of there being any free scission
12 products able to find their way from the film or material structure.
13

14 Other aspects of the present invention to some extent parallel the prior art.
15 For instance, it is desirable that the oxygen scavenging materials are
16 relatively stable (with respect to scavenging) until required. In many cases,
17 catalysis and/or triggering of any reaction is required. Photo-initiators such as
18 benzophenone may be included. Initiating or triggering by electromagnetic
19 irradiation (often in the visible through UV regions) is convenient form of
20 triggering and already used in some types of film manufacture. It is also used
21 for triggering many prior art oxygen scavengers and thus employing these
22 features and techniques of the prior art with the present invention is
23 envisaged.
24

25 As for most other oxygen scavengers relying on alkenes, some form of
26 catalyst is also required for the oxygen scavenging reactions to proceed
27 effectively. Typically transition metal catalysts are used, including their salts,
28 complexes, and other compounds. These are well documented in the prior
29 art and may also be used with the present invention as appropriate.
30

1

2

3 According to another aspect of the present invention, there is provided an
4 oxygen scavenging polymer, substantially as described above, in which the
5 reactive extrusion process comprises a transesterification process.

6

7

8

9 According to one aspect of the present invention, there is provided an oxygen
10 scavenging composition for use in or with plastics materials, said scavenger
11 comprising or including at least one cyclohexene functionality as described
12 above.

13

14 According to another aspect of the present invention, there is provided an
15 oxygen scavenging composition, as described above, which produces only
16 low levels of volatile or extractable (from a plastics material in which it is
17 incorporated) products as a consequence of oxygen scavenging.

18

19 According to another aspect of the present invention, there is provided an
20 oxygen scavenging composition, substantially as described herein which is
21 substantially stable with respect to reaction with oxygen until triggered by an
22 external event.

23

24 According to another aspect of the present invention, there is provided an
25 oxygen scavenging composition, substantially as described above, wherein
26 the external event is irradiation by actinic radiation or electron beam radiation.

27

28 According to a further aspect of the present invention, there is provided an
29 oxygen scavenging composition including an oxygen scavenger, substantially

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1 as described above, which includes one or more trigger enhancing
2 components making the scavenger susceptible to triggering from an external
3 event.

4

5 According to another aspect of the present invention, there is provided an
6 oxygen scavenging composition, substantially as described above, wherein a
7 trigger enhancing component is a photo initiator such as benzophenone or
8 substituted derivatives thereof.

9

10 According to another aspect of the present invention, there is provided an
11 oxygen scavenging composition, substantially as described above, which
12 includes the presence of one or more catalysts for the scavenging process.

13

14 According to another aspect of the present invention, there is provided an
15 oxygen scavenging composition, substantially as described above, in which
16 the catalyst is a transition metal salt, compound or complex.

17

18 According to another aspect of the present invention, there is provided an
19 oxygen scavenging composition, substantially as described above, which is in
20 the form of a plastic resin.

21

22 According to another aspect of the present invention, there is provided an
23 oxygen scavenging composition, substantially as described above, in which
24 the plastic resin is a suitable for use in the manufacture of plastics films.

25

26 According to another aspect of the present invention, there is provided an
27 oxygen scavenging composition, substantially as described above, in which
28 the plastic resin is a polyester resin.

29

-31-

1 According to another aspect of the present invention, there is provided an
2 oxygen scavenging article comprising the oxygen scavenging composition
3 described above, where the scavenging component is present as a plastic
4 film or layer thereof.

5

6 According to another aspect of the present invention, there is provided an
7 oxygen scavenger or oxygen scavenging composition, substantially as
8 described above, when used as a polymeric material of a plastic film a layer
9 thereof, and/or a coating thereof, or in a plastic material.

10

11 According to another aspect of the present invention, there is provided an
12 oxygen scavenger or oxygen scavenging composition, substantially as
13 described above, when dispersed through a plastics film, a layer thereof,
14 and/or a coating thereon, or in a plastics material.

15

16 According to a further aspect of the present invention, there is provided an
17 oxygen scavenger or oxygen scavenging composition prepared from the
18 reaction of a tetrahydrophthalic anhydride or tetrahydrophthalic acid with at
19 least one of a diol, a hydroxy compound or polyhydroxy compound, in the
20 presence of or absence of an esterification catalyst.

21

22 According to a further aspect of the present invention, there is provided an
23 oxygen scavenger or oxygen scavenging composition prepared from the
24 reaction of a tetrahydrophthalic anhydride or tetrahydrophthalic acid with at
25 least one of a diol, a hydroxy compound or polyhydroxy compound, in the
26 presence of or absence of an esterification catalyst.

27

28 According to a further aspect of the present invention there is provided an
29 oxygen scavenger or oxygen scavenging composition prepared from an ester

1 or diester of a tetrahydrophthalic anhydride, in the presence of or absence of
2 a transesterification or esterification catalyst.

3

4 According to a further aspect of the present invention, there is provided an
5 oxygen scavenger or oxygen scavenging composition substantially as
6 described above, in which the anhydride comprises 1,2,3,6 tetrahydrophthalic
7 anhydride or tetrahydrophthalic anhydride monomers derived from butadiene,
8 2,3-Dimethyl-1,3-butadiene or isoprene.

9

10 According to a further aspect of the present invention, there is provided an
11 oxygen scavenging polymer including at least one cyclohexene group
12 prepared by a reactive extrusion process.

13

14 According to the present invention, a composition is provided comprising a
15 polymeric backbone, cyclic olefinic pendent groups and linking groups linking
16 the olefinic pendent groups to the polymeric backbone.

17 Also according to the present invention, an oxygen scavenging composition is
18 provided comprising a polymeric backbone, cyclic olefinic pendent groups,
19 linking groups linking the olefinic pendent groups to the polymeric backbone
20 and a transition metal catalyst.

21 Also according to the present invention, an article of manufacture is provided
22 which is suitable as a container, the container inhibiting oxidation of contents
23 of the container by removing oxygen from the container and by inhibiting
24 ingress of oxygen into the container from outside the container, the article
25 comprising an oxygen scavenging composition which comprises a polymeric
26 backbone, cyclic olefinic pendent groups, linking groups linking the olefinic
27 pendent groups to the backbone, and a transition metal catalyst.

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1 Also according to the present invention, a layer suitable for scavenging
 2 oxygen is provided which comprises (a) a polymer backbone; (b) cyclic
 3 olefinic pendent groups; (c) linking groups linking the backbone with the
 4 pendent groups; and (d) a transition metal catalyst.

5 Also according to the present invention, a process of making a polymer
 6 material is provided, the process being selected from the group consisting of
 7 esterification, transesterification, amidation, transamidation and direct
 8 polymerization, in which the oxygen scavenging packaging material
 9 comprises a polymer backbone, cyclic olefinic pendent groups, linking groups
 10 linking the backbone with the pendent groups.

11 In a preferred embodiment of the invention, the polymeric backbone of the
 12 above compositions, article, layer and process is ethylenic and the linking
 13 groups are selected from the group consisting of:

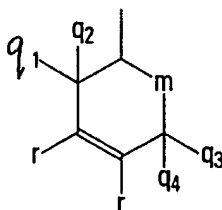
14 $-O-(CHR)_n-$; $-(C=O)-O-(CHR)_n-$; $-NH-(CHR)_n-$; $-O-(C=O)-(CHR)_n-$;

15 $-(C=O)-NH-(CHR)_n-$; and $-(C=O)-O-CHOH-CH_2-O-$;

16 wherein R is hydrogen or an alkyl group selected from the group consisting of
 17 methyl, ethyl, propyl and butyl groups and where n is an integer in the range
 18 from 1 to 12.

19 In a more preferred embodiment of the invention, the cyclic olefinic pendent
 20 groups of the above compositions, article, layer and process have the
 21 structure (II):

(II)



1

2 where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$,
3 and $-C_2H_5$; and where m is $-(CH_2)_n-$ with n being an integer in the range from 0
4 to 4; and wherein, when r is $-H$, at least one of q_1 , q_2 , q_3 and q_4 is $-H$.

5 In another preferred embodiment of the invention, the polymeric backbone of
6 the above compositions, article, layer and process comprises monomers
7 selected from the group consisting of ethylene and styrene.

8 In yet another preferred embodiment of invention, the cyclic olefinic pendent
9 groups of the above compositions, article, layer and process are grafted onto
10 the linking groups of the polymeric backbone by a esterification,
11 transesterification, amidation or transamidation reaction.

12 In still another preferred embodiment of the invention, the esterification,
13 transesterification, amidation or transamidation reaction of the above
14 compositions, article, layer and process is a solution reaction or a reactive
15 extrusion.

16 In another preferred embodiment of the invention, the esterification,
17 transesterification, amidation or transamidation reaction of the above
18 compositions, article, layer and process is catalyzed by a catalyst selected
19 from the group consisting of strong non-oxidizing acids, tertiary amines,
20 Group I alkoxides, Group IVB alkoxides, and Group IVA organometallics.

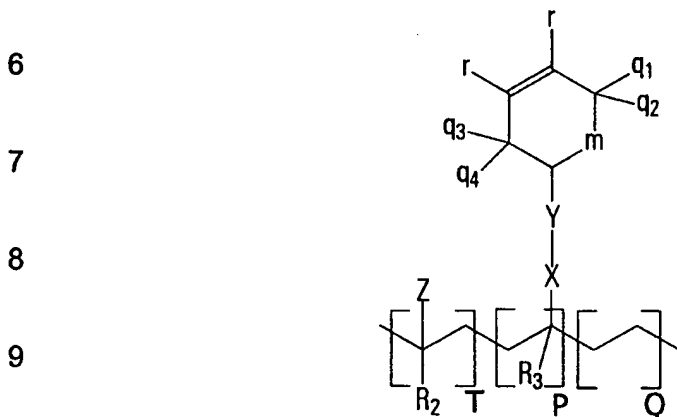
21 In yet another preferred embodiment of invention, the catalyst of the above
22 compositions, article, layer and process is selected from a group consisting of
23 toluene sulfonic acid, sodium methoxide, tetrabutyl titanate, tetraisopropyl
24 titanate, tetra-n-propyl-titanate, tetraethyl titanate, 2-hydroxy-pyridine and
25 dibutyltin dilaurate.

26

-35-

1 In still another preferred embodiment of the invention, the polymeric
 2 backbone, linking groups and cyclic olefin pendent groups of the above
 3 compositions, article, layer and process comprise repeating units, each unit
 4 having a structure (III) as follows:

5 (III)

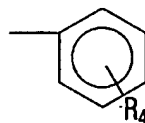


10 wherein $P+T+Q$ is 100 mol % of the total composition; P is greater than 0
 11 mol % of the tot

12 al composition; Z is selected from the group consisting of an aryl group;
 13 $-(C=O)OR_1$; $-O(C=O)R_1$; and an alkyl aryl group, structure (IV):

14 (IV)

15



16 where R_4 is selected from the group consisting of $-CH_3$, $-C_2H_5$, and $-H$; R_1 is
 17 selected from the group consisting of $-H$, $-CH_3$, $-C_2H_5$, $-C_3H_7$ and $-C_4H_9$; R_2 and
 18 R_3 are selected from the group consisting of $-H$ and $-CH_3$; X is selected from
 19 the group consisting of $-O-$, $-NH-$, $-(C=O)O-$, $-(C=O)NH-$, $-(C=O)S-$, $-O(C=O)-$
 20 and $-(CHR)_\ell-$; ℓ is an integer in the range from 1 to 6; Y is $-(CHR)_n-$, where n is
 21 an integer in the range from 0 to 12, R being selected from the group
 22 consisting of $-H$, $-CH_3$ and $-C_2H_5$; where q_1 , q_2 , q_3 , q_4 , and r are selected from
 23 the group consisting of $-H$, $-CH_3$, and $-C_2H_5$; and where m is $-(CH_2)_n-$ and

1 where n is an integer in the range from 0 to 4; and wherein when r is -H, at
2 least one of q_1 , q_2 , q_3 and q_4 is -H.

3 In another preferred embodiment of the invention, the cyclic olefinic pendent
4 groups of the above compositions, article, layer and process are selected
5 from the group consisting of cyclohexene-4-methylene radical, 1-methyl
6 cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-methylene radical,
7 5-methyl cyclohexene-4-methylene radical, 1,2-dimethyl cyclohexene-4-
8 methylene radical, 1,5-dimethyl cyclohexene-4-methylene radical,
9 2,5-dimethyl cyclohexene-4-methylene radical, 1,2,5-trimethyl cyclohexene-4-
10 methylene radical, cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-
11 ethylene radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl
12 cyclohexene-4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene radical,
13 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-4-
14 ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene radical, cyclohexene-
15 4-propylene radical, 1-methyl cyclohexene-4-propylene radical, 2-methyl
16 cyclohexene-4-propylene radical, 5-methyl cyclohexene-4-propylene radical,
17 1,2-dimethyl cyclohexene-4-propylene radical, 1,5-dimethyl cyclohexene-4-
18 propylene radical, 2,5-dimethyl cyclohexene-4-propylene radical,
19 1,2,5-trimethyl cyclohexene-4-propylene radical, cyclopentene-4-methylene
20 radical, 1-methyl cyclopentene-4-methylene radical, 3-methyl cyclopentene-4-
21 methylene radical, 1,2-dimethyl cyclopentene-4-methylene radical,
22 3,5-dimethyl cyclopentene-4-methylene radical, 1,3-dimethyl cyclopentene-4-
23 methylene radical, 2,3-dimethyl cyclopentene-4-methylene radical,
24 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
25 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-methyl
26 cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-ethylene radical,
27 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-dimethyl cyclopentene-4-
28 ethylene radical, 1,3-dimethyl cyclopentene-4-ethylene radical, 2,3-dimethyl
29 cyclopentene-4-ethylene radical, 1,2,3-trimethyl cyclopentene-4-ethylene

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1 radical, 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-
2 propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl
3 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-propylene
4 radical, 3,5-dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl
5 cyclopentene-4-propylene radical, 2,3-dimethyl cyclopentene-4-propylene
6 radical, 1,2,3-trimethyl cyclopentene-4-propylene radical, and
7 1,2,3,5-tetramethyl cyclopentene-4-propylene radical.

8 In yet another preferred embodiment of the invention, the composition of the
9 above compositions, article, layer and process is a ethylene/methyl
10 acrylate/cyclohexenyl methyl acrylate terpolymer, a cyclohexenyl methyl
11 acrylate/ethylene copolymer, a cyclohexenyl methyl methacrylate/styrene
12 copolymer, a cyclohexenyl methyl acrylate homopolymer or a methyl
13 acrylate/cyclohexenyl methyl acrylate copolymer.

14

15 In another preferred embodiment of the invention, the odor and taste
16 characteristics of products packaged with material comprised of the above
17 compositions, article, layer and process are not adulterated as a result of
18 oxidation of the composition.

19

20 In still another preferred embodiment of the invention, there is no significant
21 fragmentation of the olefinic pendent groups and linking groups from the
22 polymeric backbone as a result of oxidation of the above compositions,
23 article, layer and process.

24

25 In yet another preferred embodiment of the invention, the transition metal
26 catalyst of the above oxygen scavenging composition, article of manufacture,
27 layer and process is a metal salt.

28

1 In still another preferred embodiment of the invention, the metal in the metal
2 salt of the above oxygen scavenging composition, article of manufacture,
3 layer and process is cobalt.

4 In still another preferred embodiment of the invention, the metal salt of the
5 above oxygen scavenging composition, article of manufacture, layer and
6 process is selected from the group consisting of cobalt neodecanoate, cobalt
7 2-ethylhexanoate, cobalt oleate and cobalt stearate.

8
9 In yet another preferred embodiment of the invention, the composition of the
10 above oxygen scavenging composition, article of manufacture, layer and
11 process further comprises at least one triggering material to enhance initiation
12 of oxygen scavenging.

13
14 In still another preferred embodiment of the invention, the triggering material
15 of the above oxygen scavenging composition, article of manufacture, layer
16 and process is a photo initiator.

17
18 In a preferred embodiment of the invention, the above article of manufacture
19 is a package.

20
21 In another preferred embodiment of invention, the package article of the
22 above article of manufacture comprises a flexible film having a thickness of at
23 most 10 mil or a flexible sheet having a thickness of at least 10 mil.

24
25 In yet another preferred embodiment of the invention, the oxygen scavenging
26 system of the package article of the above article of manufacture comprises
27 at least one additional layer selected from among oxygen barrier layers,
28 polymeric selective layers, and heat seal layers.

29

1 In still another preferred embodiment of the invention, the above article of
2 manufacture is a package with a food product located within the package.

3 In yet another preferred embodiment of the invention, the above article of
4 manufacture is a package for packaging a cosmetic, chemical, electronic
5 device, pesticide or a pharmaceutical composition.

6

7 In still another preferred embodiment of the invention, a multi-layer film
8 comprises the article of the above article of manufacture and the film has at
9 least one additional functional layer.

10

11 In yet another preferred embodiment of the invention, the multi-layer film of
12 the above article of manufacture has at least one additional layer selected
13 from among oxygen barrier layers, polymeric selective barrier layers,
14 structural layers and heat seal layers.

15

16 In still another preferred embodiment of the invention, the multi-layer film of
17 the above article of manufacture has at least one additional layer which is an
18 oxygen barrier layer.

19

20 In yet another preferred embodiment of the invention, the multi-layer film of
21 the above article of manufacture further comprises at least one polymeric
22 selective barrier layer.

23

24 In still another preferred embodiment of the invention, the multi-layer film of
25 the above article of manufacture further comprises at least one heat seal
26 layer.

27

28 In yet another preferred embodiment of the invention, the multi-layer film of
29 the above article of manufacture further comprises at least one structural
30 layer.

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1 In still another preferred embodiment of the invention, the above article of
2 manufacture is a rigid container, sealing gasket, patch, container closure
3 device, bottle cap, bottle cap insert or molded or thermoformed shape.

4
5 In yet another preferred embodiment of the invention, the molded or
6 thermoformed shape of the above article of manufacture is a bottle or tray.

7
8 In still another preferred embodiment of the invention, the above layer in
9 addition comprises polymeric diluent.

10
11 In yet another preferred embodiment of the invention, the diluent of the above
12 layer is a thermoplastic polymer.

13
14 In still another preferred embodiment of the invention, the above layer is
15 adjacent to one or more additional layers.

16
17 In still another preferred embodiment of the invention, at least one of the
18 additional layers adjacent to the above layer is an oxygen barrier.

19
20 In still another preferred embodiment of the invention, the oxygen barrier of
21 the above layer comprises a member of the group consisting of poly(ethylene-
22 vinyl alcohol), polyacrylonitrile, poly(vinyl chloride), polyamides,
23 poly(vinylidene dichloride), poly(ethylene terephthalate), silica, metal foil and
24 metalized polymeric films.

25
26 In still another preferred embodiment of the invention, the one or more of said
27 additional layer or layers of the above layer is coextruded with the above
28 layer.

29

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1 In yet another preferred embodiment of the invention, the one or more of said
2 additional layer or layers of the above layer is laminated onto the above layer.

3

4 In still another preferred embodiment of the invention, the one or more of said
5 additional layer or layers of the above layer is coated onto the above layer.

6

7 In yet another preferred embodiment of the invention, the above layer is
8 flexible.

9

10 In still another preferred embodiment of the invention, the above layer is
11 transparent.

12

13 In yet another preferred embodiment of the invention, an article for packaging
14 wherein the article comprises the above layer.

15

16 In yet another preferred embodiment of the invention, the above process of
17 making the oxygen scavenging packaging material comprises the steps of:

18 (a) selecting polymers from the group consisting of styrene/maleic
19 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
20 ethylene/methacrylic acid, acrylic acid, methacrylic acid,
21 styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl
22 acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl acrylate,
23 and styrene/methyl methacrylate to form a mixture and combining the
24 polymers with an esterifying/transesterifying compound selected from
25 the group consisting of cyclohexene-4-methanol, 1-methyl cyclohexene-
26 4-methanol, 2-methyl cyclohexene-4-methanol, 5-methyl cyclohexene-4-
27 methanol, 1,2-dimethyl cyclohexene-4-methanol, 1,5-dimethyl
28 cyclohexene-4-methanol, 2,5-dimethyl cyclohexene-4-methanol,

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- 1 1,2,5-trimethyl cyclohexene-4-methanol, cyclohexene-4-ethanol,
2 1-methyl cyclohexene-4-ethanol, 2-methyl cyclohexene-4-ethanol,
3 5-methyl cyclohexene-4-ethanol, 1,2-dimethyl cyclohexene-4-ethanol,
4 1,5-dimethyl cyclohexene-4-ethanol, 2,5-dimethyl cyclohexene-4-
5 ethanol, 1,2,5-trimethyl cyclohexene-4-ethanol, cyclohexene-4-propanol,
6 1-methyl cyclohexene-4-propanol, 2-methyl cyclohexene-4-propanol,
7 5-methyl cyclohexene-4-propanol, 1,2-dimethyl cyclohexene-4-propanol,
8 1,5-dimethyl cyclohexene-4-propanol, 2,5-dimethyl cyclohexene-4-
9 propanol, 1,2,5-trimethyl cyclohexene-4-propanol, cyclopentene-4-
10 methanol, 1-methyl cyclopentene-4-methanol, 3-methyl cyclopentene-4-
11 methanol, 1,2-dimethyl cyclopentene-4-methanol, 3,5-dimethyl
12 cyclopentene-4-methanol, 1,3-dimethyl cyclopentene-4-methanol,
13 2,3-dimethyl cyclopentene-4-methanol, 1,2,3-trimethyl cyclopentene-4-
14 methanol, 1,2,3,5-tetramethyl cyclopentene-4-methanol, cyclopentene-
15 4-ethanol, 1-methyl cyclopentene-4-ethanol, 3-methyl cyclopentene-4-
16 ethanol, 1,2-dimethyl cyclopentene-4-ethanol, 3,5-dimethyl
17 cyclopentene-4-ethanol, 1,3-dimethyl cyclopentene-4-ethanol,
18 2,3-dimethyl cyclopentene-4-ethanol, 1,2,3-trimethyl cyclopentene-4-
19 ethanol, 1,2,3,5-tetramethyl cyclopentene-4-ethanol, cyclopentene-4-
20 propanol, 1-methyl cyclopentene-4-propanol, 3-methyl cyclopentene-4-
21 propanol, 1,2-dimethyl cyclopentene-4-propanol, 3,5-dimethyl
22 cyclopentene-4-propanol, 1,3-dimethyl cyclopentene-4-propanol,
23 2,3-dimethyl cyclopentene-4-propanol, 1,2,3-trimethyl cyclopentene-4-
24 propanol, and 1,2,3,5-tetramethyl cyclopentene-4-propanol;
- 25 (b) heating the polymers and esterifying/transesterifying compounds
26 selected in (a) to form a polymer melt;
- 27 (c) processing the melt in an extruder under esterification/transesterification
28 conditions with esterification/transesterification catalysts and

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1 antioxidants protecting the melt from oxidation during extrusion, so that
2 the polymer melt undergoes esterification of polymeric anhydrides with
3 cyclic olefin pendent groups, esterification of polymeric acids with cyclic
4 olefin pendent groups or exchange of alkyl groups of polymeric esters
5 with cyclic olefin pendent groups; and

6 (d) removing volatile organic products and by-products from the melt.

7 In still another preferred embodiment of the invention, the above process of
8 making the oxygen scavenging packaging material comprises the steps of:

9 (a) selecting polymers from the group consisting of styrene/maleic
10 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
11 ethylene/methacrylic acid, acrylic acid, methacrylic acid,
12 styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl
13 acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl acrylate,
14 and styrene/methyl methacrylate to form a mixture and combining the
15 polymers with an amidizing/transamidizing compound selected from the
16 group consisting of cyclohexene-4-methyl amine, 1-methyl cyclohexene-
17 4-methyl amine, 2-methyl cyclohexene-4-methyl amine, 5-methyl
18 cyclohexene-4-methyl amine, 1,2-dimethyl cyclohexene-4-methyl amine,
19 1,5-dimethyl cyclohexene-4-methyl amine, 2,5-dimethyl cyclohexene-4-
20 methyl amine, 1,2,5-trimethyl cyclohexene-4-methyl amine,
21 cyclohexene-4-ethyl amine, 1-methyl cyclohexene-4-ethyl amine,
22 2-methyl cyclohexene-4-ethyl amine, 5-methyl cyclohexene-4-ethyl
23 amine, 1,2-dimethyl cyclohexene-4-ethyl amine, 1,5-dimethyl
24 cyclohexene-4-ethyl amine, 2,5-dimethyl cyclohexene-4-ethyl amine,
25 1,2,5-trimethyl cyclohexene-4-ethyl amine, cyclohexene-4-propyl amine,
26 1-methyl cyclohexene-4-propyl amine, 2-methyl cyclohexene-4-propyl
27 amine, 5-methyl cyclohexene-4-propyl amine, 1,2-dimethyl cyclohexene-
28 4-propyl amine, 1,5-dimethyl cyclohexene-4-propyl amine, 2,5-dimethyl

- 1 cyclohexene-4-propyl amine, 1,2,5-trimethyl cyclohexene-4-propyl
2 amine, cyclopentene-4-methyl amine, 1-methyl cyclopentene-4-methyl
3 amine, 3-methyl cyclopentene-4-methyl amine, 1,2-dimethyl
4 cyclopentene-4-methyl amine, 3,5-dimethyl cyclopentene-4-methyl
5 amine, 1,3-dimethyl cyclopentene-4-methyl amine, 2,3-dimethyl
6 cyclopentene-4-methyl amine, 1,2,3-trimethyl cyclopentene-4-methyl
7 amine, 1,2,3,5-tetramethyl cyclopentene-4-methyl amine, cyclopentene-
8 4-ethyl amine, 1-methyl cyclopentene-4-ethyl amine, 3-methyl
9 cyclopentene-4-ethyl amine, 1,2-dimethyl cyclopentene-4-ethyl amine,
10 3,5-dimethyl cyclopentene-4-ethyl amine, 1,3-dimethyl cyclopentene-4-
11 ethyl amine, 2,3-dimethyl cyclopentene-4-ethyl amine, 1,2,3-trimethyl
12 cyclopentene-4-ethyl amine, 1,2,3,5-tetramethyl cyclopentene-4-ethyl
13 amine, cyclopentene-4-propyl amine, 1-methyl cyclopentene-4-propyl
14 amine, 3-methyl cyclopentene-4-propyl amine, 1,2-dimethyl
15 cyclopentene-4-propyl amine, 3,5-dimethyl cyclopentene-4-propyl
16 amine, 1,3-dimethyl cyclopentene-4-propyl amine, 2,3-dimethyl
17 cyclopentene-4-propyl amine, 1,2,3-trimethyl cyclopentene-4-propyl
18 amine, and 1,2,3,5-tetramethyl cyclopentene-4-propyl amine;
- 19 (b) heating the polymers and amidizing/transamidizing compounds selected
20 in (a) to form a polymer melt;
- 21 (c) processing the melt in an extruder under amidation/transamidation
22 conditions with amidation/transamidation catalysts and antioxidants
23 protecting the melt from oxidation during extrusion, so that the polymer
24 melt undergoes amidation of polymeric anhydrides with cyclic olefin
25 pendent groups, amidation of polymeric acids with cyclic olefin pendent
26 groups or exchange of alkyl groups of polymeric esters with cyclic olefin
27 pendent groups; and
- 28 (d) removing volatile organic products and by-products from the melt.

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1 In yet another preferred embodiment of the invention, the above process of
2 making of the oxygen scavenging packaging material comprises the steps of:
3 (a) adding to an autoclave, ethylene and a vinyl monomer comprising a
4 pendent cyclohexene;

5

6 (b) stirring the ethylene and the vinyl monomer in the autoclave to achieve a
7 mixture;

8

9 (c) adding a polymerization initiator before, during or after the stirring step;

10

11 (d) polymerizing the mixture to achieve a polymer; and

12

13 (e) isolating and purifying the polymer.

14

15 In still another embodiment of the invention, in the above process, in step (a),
16 an alpha-olefin is added to the autoclave along with the ethylene and the vinyl
17 monomer and, in step (b), the alpha-olefin is stirred with the ethylene and the
18 vinyl monomer to achieve the mixture.

19

20 The present invention relates to a non-odorous oxygen scavenging polymer
21 composition comprising: (1) monomers derived from cyclic hydrocarbon
22 moieties having at least one cyclic allylic or cyclic benzylic hydrogen and (2) a
23 transition metal oxidation catalyst. The present invention also relates to a
24 rigid container for food or beverage, the container being molded from a resin
25 comprising the above-described non-odorous oxygen scavenging polymer
26 composition. The present invention also relates to the above-described rigid
27 container further comprising a tinted ultraviolet protection layer, which may or
28 may not be the food contact layer, located between the layer comprising the
29 non-odorous oxygen scavenging composition and the inside of the rigid
30 container.

1 In a preferred embodiment of the above non-odorous oxygen scavenging
2 polymer composition, wherein the composition comprises a vinyl polymer
3 selected from the group consisting of ethylene polymer, ethylene copolymer,
4 propylene polymer, propylene copolymer, styrene polymer, styrene copolymer
5 and mixtures thereof.

6
7 In another preferred embodiment of the above non-odorous oxygen
8 scavenging polymer composition, the composition comprises condensation
9 polymers selected from the group consisting of polyesters, polyamides,
10 polycarbonate, polyurethane, polyureas and polyether.

11
12 In a more preferred embodiment of the above composition comprising
13 condensation polymers, the composition is thermoplastic.

14
15 In another more preferred embodiment of the above composition comprising
16 condensation polymers, the composition is thermoset.

17
18 In yet another more preferred embodiment of the above composition
19 comprising condensation polymers, the composition is a multilayered
20 structure with other layers being an aromatic polyester or copolyester
21 selected from the group consisting of polyethylene terephthalate,
22 polyethylene naphthalate, polypropylene terephthalate, polybutylene
23 terephthalate, polyethylene isophthalate, polycyclohexanedimethanol
24 terephthalate, polybutylene naphthalate, polycyclohexanedimethanol
25 naphthalate, and copolymers and blends thereof.

26
27 In still another more preferred embodiment of the above composition
28 comprising condensation polymers, the composition is a multilayered
29 structure with other layers being polyamides or copolyamides selected from
30 the group consisting of Nylon 6, Nylon 66, Nylon 610 and mixtures thereof.

1 In yet another more preferred embodiment of the above composition
2 comprising condensation polymers, the composition is a multilayered
3 structure with other layers being bisphenol A carbonate.

4

5 In yet another more preferred embodiment of the above composition
6 comprising condensation polymers, the composition is a multilayered
7 structure with other layers being vinylic polymers or copolymers selected
8 from the group consisting of ethylene polymer, ethylene copolymer, propylene
9 polymer, propylene copolymer, styrene polymer, styrene copolymer, acrylate
10 polymer, acrylate copolymer, vinyl chloride polymer, vinyl chloride copolymer,
11 divinyl chloride polymer, divinyl chloride copolymer, fluorinated vinyl polymer,
12 fluorinated vinyl copolymer and mixtures thereof.

13

14 In still another more preferred embodiment of the above composition
15 comprising condensation polymers, the composition is blended with an
16 aromatic polyester or copolyester selected from the group consisting of
17 polyethylene terephthalate, polyethylene naphthalate, polypropylene
18 terephthalate, polybutylene terephthalate, polyethylene isophthalate,
19 polycyclohexanedimethanol terephthalate, polybutylene naphthalate,
20 polycyclohexanedimethanol naphthalate, and copolymers and blends thereof.

21

22 In yet another more preferred embodiment of the above composition
23 comprising condensation polymers, the composition is blended with
24 polyamides or copolyamides selected from the group consisting of Nylon 6,
25 Nylon 66, Nylon 610 and mixtures thereof.

26

27 In still another more preferred embodiment of the above composition
28 comprising condensation polymers, the composition is blended with bisphenol
29 A polycarbonate.

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1 In yet another more preferred embodiment of the above composition
 2 comprising condensation polymers, the composition being a blend comprising
 3 vinylic polymers or copolymers selected from the group consisting of ethylene
 4 polymer, ethylene copolymer, propylene polymer, propylene copolymer,
 5 styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer,
 6 vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer,
 7 divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl
 8 copolymer and mixtures thereof.

9
 10 In a more preferred embodiment of the above composition comprising
 11 condensation polymers, the composition is laminated or adhering onto a
 12 substrate selected from the group consisting of paper, foil, high temperature
 13 film, metallized film, polyamide films, ethylene vinyl alcohol film, silica coated
 14 film, nylon/EVOH/nylon, oriented polypropylene, polyester film, polyethylene,
 15 polypropylene, polyester, oriented polyethylene terephthalate and cellophane.

16
 17 In another preferred embodiment of the above non-odorous oxygen
 18 scavenging polymer composition, the cyclic allylic monomers are selected
 19 from the group consisting of structure (V), structure (VI) and structure (VII):

20

21

22

23

24

25

26

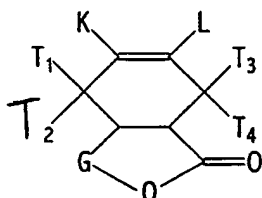
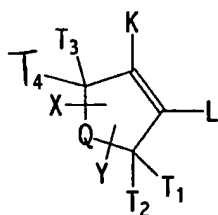
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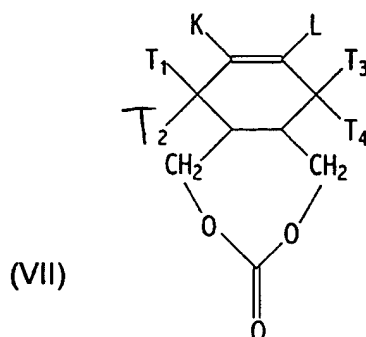
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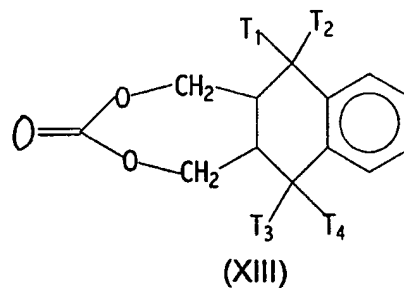
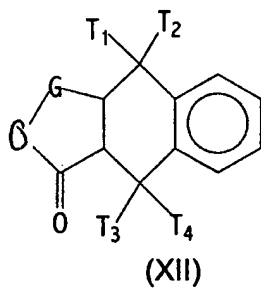
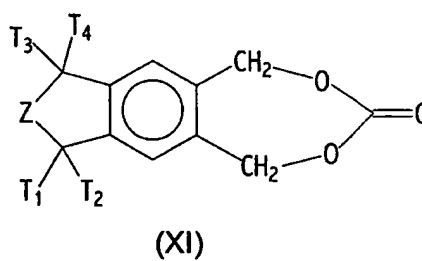
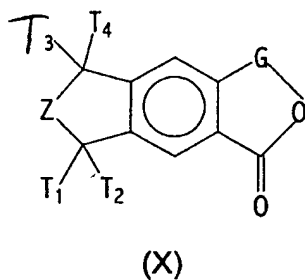
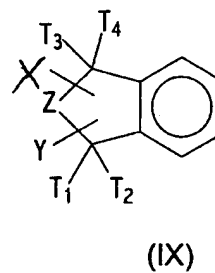
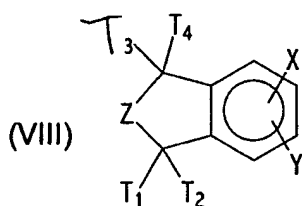
-49-



with K, L, T₁, T₂, T₃, and T₄ being selected from the group consisting of -C_qH_{2q+1} with q being an integer in the range from 0 to 12 and wherein, when either K or L is -H, at least one of T₁, T₂, T₃ and T₄ is -H; and with X and Y being selected from the group consisting of -(CH₂)_n-OH, -(CH₂)_n-NH₂, -(CH₂)_nNC=O and -(CH₂)_m-(C=O)-A with n being an integer in the range from 1 to 12 and m being an integer in the range from 0 to 12 and A being selected from the group consisting of -OH, -OCH₃, -OC₂H₅, -OC₃H₇ and halides; and Q being selected from the group consisting of -(C_tH_{2t-2}) with t being an integer in the range from 1 to 4; and with G being selected from -(C=O)- and -(C_nH_{2n+1})- with n being an integer from 0 to 12.

In yet another more preferred embodiment of the above non-odorous oxygen scavenging polymer composition, the cyclic benzylic monomers are selected from the group consisting of structure (VIII), structure (IX), structure (X), structure (XI), structure (XII), and structure (XIII)

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where X and Y are selected from the group consisting of $-(CH_2)_n-OH$,
 $-(CH_2)_n-NH_2$ and $-(CH_2)_m-(C=O)-R_1$ with n being an integer in the range

1 from 1 to 12, and with m being an integer in the range from 0 to 12 and
 2 with R₁ being selected from the group consisting of -OH, -OCH₃,
 3 -OC₂H₅, -OC₃H₇ and halides;
 4 with T₁, T₂, T₃, and T₄ being selected from the group consisting of
 5 -C_qH_{2q+1} with q being an integer in the range from 0 to 12 and at least
 6 one of T₁, T₂, T₃ and T₄ being -H;
 7 and with X and Y being selected from the group consisting of -
 8 (CH₂)_n-OH, -(CH₂)_n-NH₂, -(CH₂)_nNC=O, and -(CH₂)_m-(C=O)-A with n
 9 being an integer in the range from 1 to 12, and m being an integer in the
 10 range from 0 to 12 and A being selected from the group consisting of
 11 -OH, -OCH₃, -OC₂H₅, -OC₃H₇ and halides; and Z being selected from the
 12 group consisting of -(C_tH_{2t+2})-, -O-, -NR₂-, -S-, with t being an integer in
 13 the range from 1 to 4 and R₂ being selected from the group consisting of
 14 -OH, -OCH₃, -OC₂H₅, -OC₃H₇ and halides;
 15 and with G being selected from -(C=O)- and -(C_nH_{2n+1})- with n being an
 16 integer from 0 to 12.

17 In still another more preferred embodiment, the composition of the resin of the
 18 above-described rigid container is a single layer.

19

20 In yet another more preferred embodiment, the composition of the resin of the
 21 above-described rigid container is multilayered.

22

23 In yet another more preferred embodiment, the composition of the resin of the
 24 above-described rigid container comprises an outer air contact layer and an
 25 inner oxygen scavenging layer.

26

27 In still another more preferred embodiment, the outer air contact layer of the
 28 composition of the resin of the above-described rigid container comprises an
 29 oxygen barrier resin selected from the group consisting of polyethylene

1 terephthalate, polyethylene naphthalate and a mixture of polyethylene
2 terephthalate and polyethylene naphthalate.

3

4 In yet another more preferred embodiment, the composition of the resin of the
5 above-described rigid container further comprises at least one of an inner
6 food contact layer, a tie layer, and a tinted ultraviolet protection layer.

7

8 In still another more preferred embodiment, the inner food contact layer of the
9 composition of the resin of the above-described rigid container comprises an
10 oxygen barrier resin selected from the group consisting of polyethylene
11 terephthalate, polyethylene naphthalate and a mixture of polyethylene
12 terephthalate and polyethylene naphthalate.

13

14 In yet another more preferred embodiment, the oxygen scavenging of the
15 composition of the resin of the above-described rigid container is initiated by
16 moisture or actinic radiation.

17 In still another more preferred embodiment, the transition metal catalyst of the
18 composition of the resin of the above-described rigid container is a metal salt.

19

20 In yet another more preferred embodiment, the metal in the metal salt of the
21 transition metal catalyst of the composition of the resin of the above-
22 described rigid container is cobalt.

23

24 In still another more preferred embodiment, the metal salt of the transition
25 metal catalyst of the composition of the resin of the above-described rigid
26 container is selected from the group consisting of cobalt neodecanoate,
27 cobalt 2-ethylhexanoate, cobalt oleate and cobalt stearate.

28

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1 In yet another more preferred embodiment, the composition of the resin of the
2 above-described rigid container further comprises at least one triggering
3 material to enhance initiation of oxygen scavenging.

4

5 In still another more preferred embodiment, the triggering material of the resin
6 of the composition of the above-described rigid container is a photoinitiator.

7

8 In yet another more preferred embodiment, the photoinitiator of the resin of
9 the composition of the above-described rigid container has an ultraviolet
10 absorption window above 320 nm.

11

12 In still another more preferred embodiment, the above-described rigid
13 container is suitable for packaging oxygen sensitive drinks for extended
14 freshness and shelf life.

15

16 In yet another more preferred embodiment, the above-described rigid
17 container is suitable for packaging beer.

18

19 DESCRIPTION OF THE DRAWINGS

20 Figure 1 is a schematic showing the overall process leading to the
21 transesterification of ethylene methyl acrylate copolymers (EMAC) to give
22 modified EMAC having cyclic pendent olefins.

23 Figure 2 is a graph comparatively plotting percent oxygen in headspace at
24 4°C (initially at 1% oxygen) against time in days for two 3-layer film extrusions
25 based on Dowlex® 3010/EMCM/Dowlex® 3010 films (EMCM being an
26 acronym for ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer
27 also referred to as poly(ethylene/methyl acrylate/cyclohexene-methyl
28 acrylate)), both including the EMCM inner layer and one of them having

1 50 ppm of a non-volatile antioxidant Irganox® 1010 in the EMCM layer and
2 one of them having 100 ppm Irganox® 1010 in the EMCM layer.

3 Figure 3 is a graph comparatively plotting percent oxygen in headspace at
4 4°C (initially at 1% oxygen) against time in days for an EMCM film and two
5 EBAC blended EMCM films, one of them having 3:1 EBAC:EMCM and one of
6 them having 1:1 EBAC:EMCM.

7 Figure 4 is a graph comparatively plotting the oxygen scavenging rates and
8 capacities at 25°C in which the initial headspace oxygen was 21% (air) for an
9 EMCM film and a 2:1 EBAC:EMCM film.

10 Figure 5 is a graph showing the taste ratings in a comparative taste test
11 between food stored in two oxygen scavenging packages (EMCM and SBS)
12 and a control package (no oxygen scavenger).

13

14

15

16

DETAILED DESCRIPTION OF THE INVENTION

17

18 We have found that materials containing certain cyclohexenyl functionalities
19 are excellent oxygen absorbers when compounded with a transition metal salt
20 and optionally a photoinitiator, and that when these materials oxidize they
21 produce very low levels of oxidation byproducts. This is in marked contrast to
22 the known art, where excellent oxygen absorbers can be obtained from the
23 use of linear unsaturated compounds compound with a transition metal salt,
24 and a photoinitiator, but where the levels of oxidation byproducts are
25 excessively high. It is thought that this improvement is obtained because mild
26 oxidation of cyclohexene does not break bonds on the ring structure whilst
27 oxidation of linear unsaturated material such as linoleic acid or vegetable oil

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1 under similar conditions produces smaller molecules by chain scission. When
2 incorporated into polymers, the cyclohexene containing systems are found to
3 produce considerably less volatile byproducts than the linear unsaturated
4 materials.

5 The compositions of this invention are significantly cleaner than those
6 described in the prior art, they do not require the use of high levels of adjuncts
7 to absorb the undesirable byproducts. Such absorbent additives are known in
8 the art, for example see U.S. 5,834,079 and U.S. 08/857,276. It is also well
9 known in the art that such additives (zeolites and silicas) adversely affect the
10 haze and clarity of packaging structures.

11

12 The oxygen scavenging compositions consist of:

13 (a) a polymer or lower molecular weight material containing substituted
14 cyclohexene functionality according to the following structure (I):

15

16

17

18

19

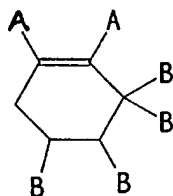
(I)

20

21

22

23



24 where A may be hydrogen or methyl and either one or two of the B groups is
25 a heteroatom containing linkage which attaches the cyclohexene ring to
26 the said material. The remaining B groups are hydrogen or methyl;

27

28 (b) a transition metal catalyst;

1

2 (c) an optional photoinitiator.

3

4 The compositions may be polymeric in nature or they may be lower molecular
5 weight materials. In either case, they may be blended with further polymers
6 or other additives. In the case of low molecular weight materials they will
7 most likely be compounded with a carrier resin before use. The following
8 examples represent some applications of various embodiments of the present
9 invention currently envisaged by the patentee. These examples are not
10 meant to be limiting nor exhaustive but merely illustrative of how the present
11 invention may be used, or applied to address problems associated with the
12 prior art.

13

14

15 The compositions of this invention can be used in a wide range of packaging
16 materials, and are not restricted to flexible packaging films and articles such
17 as pouches produced from such films. The compositions may also be used in
18 the preparation of rigid and semi rigid packaging materials. Typical rigid and
19 semi rigid articles include plastic, paper or cardboard cartons, bottles such as
20 juice containers, thermoformed trays, or cups with wall thicknesses of about
21 100 to 2000 microns. The walls of such articles comprise single or multiple
22 layers of materials. The compositions can be used as the sole polymeric
23 material from which one or more layers of a film are formed (i.e., the film can
24 be a multilayer film having, for example, a gas barrier layer, a seal layer, etc.),
25 it can be blended with other polymeric oxygen scavenging agents (such as
26 polybutadiene) or it can be blended with one or more diluent polymers which
27 are known to be useful in the formation of packaging film materials and which
28 often can render the resultant film more flexible and/or processable. Suitable
29 diluent polymers include, but are not limited to, polyethylene such as, for
30 example, low density polyethylene, very low density polyethylene, ultra-low

1 density polyethylene, high density polyethylene, and linear low density
2 polyethylene; polyesters such as, for example, polyethylene terephthalate
3 (PET); polyvinyl chloride (PVC); polyvinylidene chloride (PVDC); and ethylene
4 copolymers such as ethylene/vinyl acetate copolymer, ethylene/alkyl
5 (meth)acrylate copolymers, ethylene/(meth)acrylic acid copolymers, and
6 ionomers. Blends of different diluent polymers also can be used.

7

8 The compositions of this invention can also be used in non integral packaging
9 components such as coatings, bottle cap liners, adhesive and non adhesive
10 sheet inserts, coupons, gaskets, sealants or fibrous mass inserts.

11

12 Generally, the foregoing diluent polymers are semi-crystalline materials.

13 Advantageously, the polymeric component of the composition of the present
14 invention can be crystalline or semi-crystalline at ambient conditions and,
15 accordingly, can be especially compatible with such diluent polymers.

16 Selection of a particular diluent polymer(s) depends largely on the article to
17 be manufactured and the end use thereof. For instance, certain polymers are
18 known by the ordinarily skilled artisan to provide clarity, cleanliness, barrier
19 properties, mechanical properties, and/or texture to the resultant article.

20

21 In combination with the polymeric component, the oxygen scavenging
22 composition of the present invention includes a transition metal compound as
23 an oxygen scavenger catalyst. The transition metal catalyst can be a slat
24 which includes a metal selected from the first, second, or third transition
25 series of the Periodic Table. The metal preferably is Rh, Ru, or one of the
26 elements in the series of Sc to Zn (i.e., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and
27 Zn), more preferably at least one of Mn, Fe, Co, Ni, and Cu, and most
28 preferably Co. Suitable anions for such salts include, but are not limited to,
29 chloride, acetate, oleate, stearate, palmitate, 2-ethylhexanoate,
30 neodecanoate, and naphthenate. Representative salts include cobalt (II)

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1 2-ethylhexanoate, cobalt oleate, and cobalt (II) neodecanoate. (The metal
2 salt also can be an ionomer, in which case a polymeric counterion is
3 employed.)

4

5 When used in forming a packaging article, the oxygen scavenging
6 composition of the present invention can include only the above-described
7 polymers and a transition metal catalyst. However, photoinitiators can be
8 added to further facilitate and control the initiation of oxygen scavenging
9 properties. Adding a photoinitiator or a blend of photoinitiators to the oxygen
10 scavenging composition can be preferred, especially where antioxidants have
11 been added to prevent premature oxidation of the composition during
12 processing and storage.

13

14 Suitable photoinitiators are known to those skilled in the art. See, e.g., PCT
15 Publication WO 97/07161, WO 97/44364, WO 98/51758, and WO 98/51759,
16 the teachings of which are incorporated herein by reference as if set forth in
17 full. Specific examples of suitable photoinitiators include, but are not limited
18 to, benzophenone, and its derivatives, such as methoxybenzophenone,
19 dimethoxybenzophenone, dimethylbenzophenone, diphenoxybenzophenone,
20 allyloxybenzophenone, diallyloxybenzophenone, dodecyloxybenzophenone,
21 dibenzosuberone, 4,4'-bis(4-isopropylphenoxy)benzophenone,
22 4-morpholinobenzophenone, 4-aminobenzophenone, tribenzoyl
23 triphenylbenzene, tritoluoyl triphenylbenzene, 4,4'-bis(dimethylamino)-
24 benzophenone, acetophenone and its derivatives, such as, o-methoxy-
25 acetophenone, 4'-methoxyacetophenone, valerophenone, hexanophenone,
26 α -phenyl-butyrophenone, p-morpholinopropiophenone, benzoin and its
27 derivatives, such as, benzoin methyl ether, benzoin butyl ether, benzoin
28 tetrahydropyranyl ether, 4-o-morpholinodeoxybenzoin, substituted and
29 unsubstituted anthraquinones, α -tetralone, acenaphthenequinone,
30 9-acetylphenanthrene, 2-acetyl-phenanthrene, 10-thioxanthenone, 3-acetyl-

1 phenanthrene, 3-acetylindole, 9-fluorenone, 1-indanone,
2 1,3,5-triacetylbenzene, thioxanthen-9-one, isopropylthioxanthen-9-one,
3 xanthene-9-one, 7-H-benz[de]anthracen-7-one, 1'-acetonaphthone,
4 2'-acetonaphthone, acetonaphthone, benz[de]anthracen-7-one,
5 1'-acetonaphthone, 2'-acetonaphthone, acetonaphthone, benz[a]anthracene-
6 7,12-dione, 2,2-dimethoxy-2-phenylacetophenone,
7 α,α -diethoxyacetophenone, α,α -dibutoxyacetophenone, 4-benzoyl-4'-
8 methyl(diphenyl sulfide) and the like. Single oxygen-generating
9 photosensitizers such as Rose Bengal, methylene blue, and
10 tetraphenylporphine as well as polymeric initiators such as poly(ethylene
11 carbon monoxide) and oligo[2-hydroxy-2-methyl-1-[4-(1-
12 methylvinyl)phenyl]propanone] also can be used. However, photoinitiators
13 are preferred because they generally provide faster and more efficient
14 initiation. When actinic radiation is used, photoinitiators can provide initiation
15 at longer wavelengths which are less costly to generate and present less
16 harmful side effects than shorter wavelengths.

17
18 When a photoinitiator is present, it can enhance and/or facilitate the initiation
19 of oxygen scavenging by the composition of the present invention upon
20 exposure to radiation. The amount of photoinitiator can depend on the
21 amount and type of cyclic unsaturation present in the polymer, the
22 wavelength and intensity of radiation used, the nature and amount of
23 antioxidants used, and the type of photoinitiator used. The amount of
24 photoinitiator also can depend on how the scavenging composition is used.
25 For instance, if a photoinitiator-containing composition is in a film layer, which
26 underneath another layer is somewhat opaque to the radiation used, more
27 initiator might be needed. However, the amount of photoinitiator used for
28 most applications ranges from about 0.01 to about 10% (By wt.) of the total
29 composition. Oxygen scavenging can be initiated by exposing an article

1 containing the composition of the present invention to actinic or electron
2 beam radiation, as described below.

3

4 One or more antioxidants can be incorporated into the scavenging
5 composition of the present invention to retard degradation of the components
6 during compounding and film formation. Although such additives prolong the
7 induction period for oxygen scavenging activity to occur in the absence of
8 irradiation, the layer or article (and any incorporated photoinitiator) can be
9 exposed to radiation at the time oxygen scavenging properties are required.
10 Suitable antioxidants include 2,6-di(t-butyl)-4-methylphenol(BHT),
11 2,2'-methylene-bis(6-t-butyl-p-cresol), triphenylphosphite, tris-
12 (nonylphenyl)phosphite, dilaurylthiodipropionate, vitamin E (α -tocopherol),
13 octadecyl 3,5,-di-tert-butyl-4-hydroxyhydrocinnamate,
14 tetrakis[methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]methane and
15 the like.

16

17 When an antioxidant is included as part of the composition of the present
18 invention, it preferably is present in an amount which prevents oxidation of the
19 components of the oxygen scavenging composition as well as other materials
20 present in a resultant blend during formation and processing; however, the
21 amount preferably is less than that which interferes with the scavenging
22 activity of the resultant layer, film, or article after initiation has occurred. The
23 amount needed in a given composition can depend on the components
24 present therein, the particular antioxidant used, the degree and amount of
25 thermal processing used to form the shaped article, and the dosage and
26 wavelength of radiation applied to initiate oxygen scavenging. Typically, such
27 antioxidant(s) are used in an amount of from about 0.01 to about 1% (by wt.).

28

29 Other additives that also can be included in the oxygen scavenging
30 composition of the present invention include, but are not necessarily limited

1 to, fillers, pigments, dyestuffs, processing aids, plasticizers, antifog agents,
2 antiblocking agents, and the like.

3

4 The amounts of the components used in the oxygen scavenging composition
5 of the present invention can affect the use and effectiveness of this
6 composition. Thus, the amounts of polymer, transition metal catalyst, and
7 any photoinitiator, antioxidant, polymeric diluents, additives, etc., can vary
8 depending on the desired article and its end use. For example, one of the
9 primary functions of the polymer described above is to react irreversibly with
10 oxygen during the scavenging process, while a primary function of the
11 transition metal catalyst is to facilitate this process. Thus, to a large extent,
12 the amount of polymer present affects the oxygen scavenging capacity of the
13 composition, i.e., the amount of oxygen that the composition can consume,
14 while the amount of transition metal catalyst affects the rate at which oxygen
15 is consumed as well as the induction period.

16

17 The composition of the present invention can provide oxygen scavenging
18 properties at a desirable rate and capacity while having good processing and
19 compatibility properties relative to compositions including conventional non-
20 cyclic ethylenically unsaturated polymers. Thus, the present composition can
21 be used to provide, by itself or as a blend with diluent film-forming polymers
22 such as polyolefins and the like, a packaging material or film that can be
23 manufactured and processed easily. Further, the subject oxygen scavenging
24 composition will deplete the oxygen within a package cavity without
25 substantially detracting from the color, taste, and/or odor of the product
26 contained therein.

27

28 The amount of the polymeric scavenging component contained in the subject
29 composition can range from about 1 to almost about 100%, preferably from
30 about 5 to about 97.5%, more preferably from about 10 to 95%, even more

1 preferably from about 15 to about 92.5%, still more preferably from about 20
2 to about 90%, (with all the foregoing percentages being by weight) of the
3 composition or layer made therefrom. Typically, the amount of transition
4 metal catalyst can range from 0.001 to 1% (by wt.) of the scavenging
5 composition, based on the metal content only (i.e., excluding ligands,
6 counterions, etc.). Where one or more other scavenging compounds and/or
7 diluent polymers are used as part of the composition, such other materials
8 can make up as much as 99%, preferably up to about 75%, by weight of the
9 scavenging composition. Any further additives employed normally do not
10 make up more than 10%, preferably no more than about 5%, by weight of the
11 scavenging composition.

12
13 As indicated above, the composition of the present invention can be used to
14 produce a scavenging monolayer film, a scavenging layer of a multilayer film,
15 or other articles for a variety of packaging applications. Single layer articles
16 can be prepared readily by extrusion processing. Multilayer films typically are
17 prepared using coextrusion, coating, lamination or processing. Multilayer
18 films typically are prepared using coextrusion, coating, lamination or
19 extrusion/lamination as taught in, for example, U.S. Patents 5,350,622 and
20 5,529,833, the teachings of which are incorporated herein by reference as if
21 set forth in full. At least one of the additional layers of multilayer article can
22 include a material having a permeance to oxygen of no more than about
23 $5.8 \times 10^{-8} \text{ cm}^3/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$ (i.e., about $500 \text{ cm}^3/\text{m}^2 \cdot 24 \text{ hours} \cdot \text{atm}$) at about 25°C.
24 Polymers which are commonly used in such oxygen barrier layers include
25 poly(ethylene/vinyl alcohol), poly(vinyl alcohol), polyacrylonitrile, PVC, PVDC,
26 PET, silica, and polyamides such as nylon 6, MXD6, nylon 66, as well as
27 various amide copolymers. (Metal foil layers can also provide oxygen barrier
28 properties.) Other additional layers can include on or more layers which are
29 permeable to oxygen. In one preferred packaging construction, especially
30 flexible packages for food, the layers can include (in order starting from the

1 outside of the package to the innermost layer of the package) (a) an oxygen
2 barrier layer, (b) a scavenging layer, i.e. one that includes the scavenging
3 composition described supra, and optionally, (c) an oxygen permeable layer.
4 Control of the oxygen barrier property of layer (a) provides a means to
5 regulate the scavenging life of the package by limiting the rate of oxygen
6 entry to the scavenging layer (b), thus limiting the rate of consumption of
7 scavenging capacity. Control of the oxygen permeability of layer (c) provides
8 a means to set an upper limit on the rate of oxygen scavenging for the overall
9 structure independent of the composition of scavenging layer (b). This can
10 serve the purpose of extending the handling lifetime of the film in the
11 presence of air prior to sealing of the package. Furthermore, layer (c) can
12 provide a barrier to migration of the individual components or byproducts of
13 the scavenging layer into the package interior. The term "exposed to the
14 interior" refers to a portion of a packaging article having the subject
15 scavenging composition which is either directly exposed or indirectly exposed
16 (via layers which are O₂ permeable) to the interior cavity having oxygen
17 sensitive product. Even further, layer (c) also can improve the heat
18 sealability, clarity, and/or resistance to blocking of the multilayer film. Further
19 additional layers such as the layers, easy open layers, and seal layers can
20 also be used. Polymers typically used in such tie layers include, for example,
21 anhydride functional polyolefins.

22
23 The method of the present invention includes exposing the above-described
24 composition to a package cavity having an oxygen sensitive product therein.
25 A preferred embodiment provides for including a photoinitiator as part of the
26 subject composition and subjecting a film, layer, or article that includes such a
27 composition to radiation so as to initiate oxygen scavenging at desired rates.
28 The thermal radiation used in heating and processing polymers typically used
29 in packaging films (e.g., 100-250°C) advantageously does not trigger the
30 oxygen scavenging reaction.

1
2 The initiating radiation preferably is actinic, e.g., UV or visible light having a
3 wavelength of from about 200 to about 750 nm, preferably of from about 200
4 to 600 nm, and most preferably from about 200 to 400 nm. Such light can be
5 delivered in a continuous or pulsed manner. The layer, film, etc., containing
6 the oxygen scavenging composition preferably is exposed to such radiation
7 until it receives at least about 1 J/g of radiation, more preferably until it
8 receives a dose in the range of about 10 to about 2000 J/g. The radiation
9 also can be electron-beam radiation at a dosage of at least about 2 kiloGray
10 (kG), preferably from about 10 to about 100 kG. Other potential sources of
11 radiation include ionizing radiation such as gamma, X-ray, and corona
12 discharge. Duration of exposure depends on several factors including, but
13 not limited to, the amount and type of photoinitiator present, thickness of the
14 layers to be exposed, thickness and opacity of intervening layers, amount of
15 any antioxidant present, and the wavelength and intensity of the radiation
16 source.

17
18 When using oxygen scavenging layers or articles, irradiation can occur during
19 or after the layer or article is prepared. If the resulting layer or articles is to be
20 used to package an oxygen sensitive product, exposure can be just prior to,
21 during, or after packaging. For best uniformity of radiation, exposure
22 preferably occurs at a processing stage where the layer or article is in the
23 form of a flat sheet. For further information on initiation via irradiation, the
24 reader is directed to PCT publications WO 98/05555 and WO 98/05703, as
25 well as PCT 97/13598, 97/13370, 97/13369, the teachings of which are
26 incorporated herein by reference.

27
28 Determining the oxygen scavenging rate and capacity of a given oxygen
29 scavenging composition contemplated for a particular use can be beneficial.
30 To determine the rate, the time elapsed before the scavenger depletes a

1 certain amount of oxygen from a sealed container is measured. In some
2 instances, the rate can be determined adequately by placing a film containing
3 the desired scavenging composition in an air-tight, sealed container of an
4 oxygen containing atmosphere, e.g., air which typically contains 20.6% (by
5 vol.) O₂. Over time, samples of the atmosphere inside the container are
6 removed to determine the percentage of oxygen remaining. (Usually, the
7 specific rates obtained vary under different temperature and atmospheric
8 conditions. Atmospheres having lower initial oxygen content and/or
9 maintained under low temperature conditions provide a more stringent test of
10 the scavenging ability and rate of a composition. The rates which follow are
11 at room temperature and one atmosphere of air, unless otherwise specified.)
12 When an active oxygen barrier is needed, a useful scavenging rate can be as
13 low as about 0.05 cm³ oxygen per gram of the polymer in the scavenging
14 composition per day in air at 25°C and at 1 atm (101.3 kPa). However, in
15 most instances, the present composition has a rate equal to or greater than
16 about 5.8 x 10⁻⁸ cm³/g•s (0.5 cm³/g•day), even up to or greater than about
17 5.8 x 10⁻⁵ cm³/g•s (5 cm³/g•day). Further, films or layers including the subject
18 composition are capable of a scavenging rate greater than about
19 1.2 x 10⁻⁴ cm³/m²•s (10 cm³/m²•day) and under some conditions, greater than
20 about 2.9 x 10⁻⁴ cm³/m²•s (25 cm³/m²•day). (Generally, films or layers
21 generally deemed suitable for use as an active oxygen barrier can have a
22 scavenging rate as low as 1.2 x 10⁻⁵ cm³/m²•s (1 cm³/m²•day) when measured
23 in air at 25°C and 101 kPa (1 atm). Such rates make those layers suitable for
24 scavenging oxygen from within a package, as well as suitable for active
25 oxygen barrier applications.

26

27 When the method of the present invention is to be used in an active oxygen
28 barrier application, the initiated oxygen scavenging activity, in combination
29 with any oxygen barriers, preferably creates an overall oxygen permeance of
30 less than about 1.1 x 10⁻¹⁰ cm³/m²•s•Pa (1.0 cm³/m²•day•atm) at 25°C. The

1 oxygen scavenging capacity preferably is such that this value is not exceeded
2 for at least two days.

3

4 Once scavenging has been initiated, the scavenging composition, layer, or
5 article prepared therefrom preferably is able to scavenge up to its capacity,
6 i.e., the amount of oxygen which the scavenger is capable of consuming
7 before it becomes ineffective. In actual use, the capacity required for a given
8 application can depend on the quantity of oxygen initially present in the
9 package, the rate of oxygen entry into the package in the absence of the
10 scavenging property, and the intended shelf life for the package. When using
11 scavengers that include the composition of the present invention, the capacity
12 can be as low as 1 cm³/g, but can be 50 cm³/g or higher. When such
13 scavengers are in a layer of a film, the layer preferably has an oxygen
14 capacity of at least about 9.8 cm³/m² per μm thickness (1200 cm³/m² per mil).

15

16 The composition of the present invention has been found to be capable of
17 providing a film, layer or article which substantially retains its physical
18 properties (e.g., tensile strength and modulus) even after substantial oxygen
19 scavenging has occurred. In addition, the present composition does not
20 provide significant amounts of byproducts and/or effluents, which can impart
21 an undesired taste, color, and/or odor to the packaged product.

22

23 This invention relates to an oxygen scavenging polymer composition
24 comprising cyclic allylic pendent groups which can be used in oxygen
25 scavenging packaging material which have either no or low volatile oxidation
26 by-products. Minimizing volatile by-products reduces the problem of
27 organoleptics in oxygen scavenging food packaging.

28 The polymer composition with cyclic allylic pendent groups can be made by
29 grafting methyl cyclohex-1-ene-4-methanol, cyclohex-1-ene-4-methanol

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1 (1,2,5,6-tetrahydrobenzyl alcohol) and cyclohex-1-ene-4-propanol onto EMAC
2 resins by transesterification of the corresponding alcohols or transamidation
3 of the corresponding amines with the methyl esters on EMAC to give modified
4 EMAC having pendent cyclic olefins (see Figure 1). The composition can
5 also be made by direct polymerization.

6 The esterification, transesterification, amidation or transamidation reaction
7 can be a solution reaction or by reactive extrusion. The catalysts can be any
8 one of strong non-oxidizing acids, tertiary amines, Group I alkoxides,
9 Group IVB alkoxides and Group IVA metal organics. The level of olefin in the
10 final products can be controlled by the level of transesterification and the
11 methyl ester content of the start EMAC. The molecular weight of the
12 polymers largely depends on the molecular weight of the EMAC feeds.

13 In a preferred embodiment, these products are combined with a transition-
14 metal salt to catalyze the oxygen scavenging properties of the materials. A
15 transition-metal salt, as the term is used here, comprises an element chosen
16 from the first, second and third transition series of the periodic table of the
17 elements, particularly one that is capable of promoting oxidation reactions.
18 This transition-metal salt is in a form which facilitates or imparts scavenging of
19 oxygen by the composition of this invention. A plausible mechanism, not
20 intended to place limitations on this invention, is that the transition element
21 can readily inter-convert between at least two oxidation states and facilitates
22 formation of free radicals. Suitable transition-metal elements include, but are
23 not limited to, manganese II or III, iron II or III, cobalt II or III, nickel II or III,
24 copper I or II, rhodium II, III or IV, and ruthenium. The oxidation state of the
25 transition-metal element when introduced into the composition is not
26 necessarily that of the active form. It is only necessary to have the transition-
27 metal element in its active form at or shortly before the time that the
28 composition is required to scavenge oxygen. The transition-metal element is

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1 preferably iron, nickel or copper, more preferably manganese and most
2 preferably cobalt.

3 Suitable counter-ions for the transition metal element are organic or inorganic
4 anions. These include, but are not limited to, chloride, acetate, stearate,
5 oleate, palmitate, 2-ethylhexanoate, citrate, glycolate, benzoate,
6 neodecanoate or naphthenate. Organic anions are preferred. Particularly
7 preferable salts include cobalt 2-ethylhexanoate, cobalt benzoate, cobalt
8 stearate, cobalt oleate and cobalt neodecanoate. The transition-metal
9 element may also be introduced as an ionomer, in which case a polymeric
10 counter-ion is employed.

11 The composition of the present invention when used in forming a oxygen
12 scavenging packaging article can be composed solely of the above described
13 polymer and transition metal catalyst. However, components, such as
14 photoinitiators, can be added to further facilitate and control the initiation of
15 oxygen scavenging properties. For instance, it is often preferable to add a
16 photoinitiator, or a blend of different photoinitiators, to the oxygen scavenger
17 compositions, especially when antioxidants are included to prevent premature
18 oxidation of that composition during processing.

19 Suitable photoinitiators are well known in the art. Such photoinitiators are
20 discussed in U.S. Patent No. 5,211,875. It is also discussed in U.S. Patent
21 Application Serial No. 08/857,325, in which some of the present inventors
22 were contributing inventors and which is incorporated herein by reference.
23 Specific examples include, but are not limited to, benzophenone, o-methoxy-
24 benzophenone, acetophenone, o-methoxy-acetophenone,
25 acenaphthenequinone, methyl ethyl ketone, valerophenone, hexanophenone,
26 α -phenyl-butyrophenone, p-morpholinopropiophenone, dibenzosuberone,
27 4-morpholinobenzophenone, benzoin, benzoin methyl ether,
28 4-o-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone,

1 4'-methoxyacetophenone, substituted and unsubstituted anthraquinones,
2 α -tetralone, 9-acetylphenanthrene, 2-acetyl-phenanthrene,
3 10-thioxanthenone, 3-acetyl-phenanthrene, 3-acetylindole, 9-fluorenone,
4 1-indanone, 1,3,5-triacetylbenzene, thioxanthen-9-one, xanthene-9-one,
5 7-H-benz[de]anthracen-7-one, benzoin tetrahydropyranyl ether,
6 4,4'-bis(dimethylamino)-benzophenone, 1'-acetonaphthone,
7 2'-acetonaphthone, acetonaphthone and 2,3-butanedione,
8 benz[a]anthracene-7,12-dione, 2,2-dimethoxy-2-phenylacetophenone,
9 α,α -diethoxy-acetophenone, α,α -dibutoxyacetophenone, etc. Singlet oxygen
10 generating photosensitizers such as Rose Bengal, methylene blue, and
11 tetraphenyl porphine may also be employed as photoinitiators. Polymeric
12 initiators include polyethylene carbon monoxide and oligo[2-hydroxy-2-
13 methyl-1-[4-(1-methylvinyl)phenyl]propanone]. Use of a photoinitiator is
14 preferable because it generally provides faster and more efficient initiation.

15 When a photoinitiator is used, its primary function is to enhance and facilitate
16 the initiation of oxygen scavenging upon exposure to radiation. The amount
17 of photoinitiator can vary. In many instances, the amount will depend on the
18 amount and type of oxygen scavenging polymer in the present invention, the
19 wavelength and intensity of radiation used, the nature and amount of
20 antioxidants used, as well as the type of photoinitiator used. The amount of
21 photoinitiator also depends on how the scavenging composition is used. For
22 instance, if the photoinitiator-coating composition is placed underneath a layer
23 which is somewhat opaque to the radiation used, more initiator may be
24 needed. For most purposes, however, the amount of photoinitiator, when
25 used, will be in the range of 0.01 to 10% by weight of the total composition.
26 The initiating of oxygen scavenging can be accomplished by exposing the
27 packaging article to actinic or electron beam radiation, as described below.

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1 Antioxidants may be incorporated into the scavenging compositions of this
2 invention to control degradation of the components during compounding and
3 shaping. An antioxidant, as defined herein, is any material which inhibits
4 oxidative degradation or cross-linking of polymers. Typically, such
5 antioxidants are added to facilitate the processing of polymeric materials
6 and/or prolong their useful shelf-life.

7 Antioxidants such as Vitamin E, Irganox® 1010, Irganox® 1076,
8 2,6-di(t-butyl)-4-methyl-phenol(BHT), 2,6-di(t-butyl)-4-ethyl-phenol (BHEB),
9 2,2'-methylene-bis(6-t-butyl-p-cresol), triphenylphosphite,
10 tris-(nonylphenyl)phosphite and dilaurylthiodipropionate would be suitable for
11 use with this invention.

12 When an antioxidant is included as part of the present composition, it should
13 be used in amounts which will prevent oxidation of the scavenger
14 composition's components as well as other materials present in a resultant
15 blend during formation and processing but the amount should be less than
16 that which would interfere with the scavenging activity of the resultant layer,
17 film or article. The particular amount needed will depend on the particular
18 components of the composition, the particular antioxidant used, the degree
19 and amount of thermal processing used to form the shaped article, and the
20 dosage and wavelength of radiation applied to initiate oxygen scavenging and
21 can be determined by conventional means. Typically, they are present in
22 about 0.01 to 1% by weight.

23 Other additives which may also be included in oxygen scavenger layers
24 include, but are not necessarily limited to, fillers, pigments, dyestuffs,
25 stabilizers, processing aids, plasticizers, fire retardants, anti-fog agents, etc.

26 The amounts of the components which are used in the oxygen scavenging
27 compositions, or layers have an effect on the use, effectiveness and results of

1 this method. Thus, the amounts of polymer, transition metal catalyst and any
2 photoinitiator, antioxidant, polymeric diluents and additives, can vary
3 depending on the article and its end use.

4 For instance, one of the primary functions of the polymer described above is
5 to react irreversibly with oxygen during the scavenging process, while the
6 primary function of the transition metal catalyst is to facilitate this process.
7 Thus, to a large extent, the amount of polymer present will affect the oxygen
8 scavenging capacity of the composition, i.e., affect the amount of oxygen that
9 the composition can consume. The amount of transition metal catalyst will
10 affect the rate at which oxygen is consumed. Because it primarily affects the
11 scavenging rate, the amount of transition metal catalyst may also affect the
12 onset of oxygen scavenging (induction period).

13 It has been found that the subject polymers, when used as part of the present
14 composition, provide oxygen scavenger properties at desirable rate and
15 capacity while causing the composition to have enhanced processability and
16 compatibility properties over conventional ethylenically unsaturated polymers.
17 Thus, the present composition can be used to provide, by itself or as a blend
18 with diluent polymers, such as polyolefins and the like, a packaging material
19 or film having enhanced processability properties. Further, the present
20 composition consumes and depletes the oxygen within a package cavity
21 without substantially detracting from the color, taste and/or odor of the
22 product contained within the package cavity.

23 The amount of the above-described polymer contained as part of the present
24 composition may range from about 1 to 100% by weight of the composition or
25 layer composed of said composition in which both polymer and transition
26 metal catalyst are present (hereinafter referred to as the "scavenging
27 composition", e.g., in a coextruded film or container, the scavenging
28 composition would comprise the particular layer(s) in which both the

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1 copolymer and transition metal catalyst components are present together).
2 Typically, the amount of transition metal catalyst may range from 0.001 to 1%
3 (10 to 10,000 ppm) of the scavenging composition, based on the metal
4 content only (excluding ligands, counterions, etc.). In the event the amount of
5 transition metal catalyst is less than 1%, it follows that the polymer and any
6 additives will comprise substantially all of the remainder of the composition.
7 The polymer of the present invention may further be combined with other
8 polymeric oxygen scavenger agents.

9 Any further additives employed normally will not comprise more than 10% of
10 the scavenging composition, with preferable amounts being less than 5% by
11 weight of the scavenging composition.

12 Optionally, the compositions and process of this invention can include
13 exposure of the polymer containing the oxygen scavenging-promoting
14 transition metal to actinic radiation to reduce the induction period, if any,
15 before oxygen scavenging commences. A method is known for initiating
16 oxygen scavenging by exposing a film comprising an oxidizable organic
17 compound and a transition metal catalyst to actinic radiation. A composition
18 of the present invention which has a long induction period in the absence of
19 actinic radiation but a short or non-existent induction period after exposure to
20 actinic radiation is particularly preferred. They maintain a high capability for
21 scavenging oxygen upon activation with actinic radiation. Thus, oxygen
22 scavenging can be activated when desired.

23 The radiation used in this method should be actinic, e.g., ultraviolet or visible
24 light having a wavelength of about 200 to 750 nanometers (nm), and
25 preferably having a wavelength of about 200 to 600 nm, and most preferably
26 from about 200 to 400 nm. When employing this method, it is preferable to
27 expose the oxygen scavenger to at least 0.01 Joule per gram of scavenging
28 composition. A typical amount of exposure is in the range of 10 to

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1 2000 Joules per gram. The radiation can also be an electron beam radiation
2 at a dosage of about 2 to 200 kiloGray, preferably about 10 to 100 kiloGray.
3 Other sources of radiation include ionizing radiation such as gamma, X-rays
4 and corona discharge. The duration of exposure depends on several factors
5 including, but not limited to, the amount and type of photoinitiator present,
6 thickness of the layers to be exposed, thickness and opacity of intervening
7 layers amount of any antioxidant present, and the wavelength and intensity of
8 the radiation source. The radiation provided by heating of polyolefin and the
9 like polymers (e.g., 100-250°C) during processing does not cause triggering.

10 Oxygen-scavenging compositions of the present invention are useful in many
11 ways. The compositions can be dispersed as small particles for absorbing
12 oxygen or can be coated onto materials such as metallic foil, polymer film,
13 metalized film, paper or cardboard to provide, in some embodiments,
14 scavenging properties and/or adhesive properties. The compositions are also
15 useful in making articles such as single or multi-layer rigid thick-walled plastic
16 containers or bottles (typically, between 5 and 100 mils in thickness) or in
17 making single or multi-layer flexible films, especially thin films (less than
18 5 mils, or even as thin as about 0.25 mil). Some of the compositions of the
19 present invention are easily formed into films using well-known means.
20 These films can be used alone or in combination with other films or materials.

21 The compositions of the present invention may be further combined with one
22 or more polymers, such as thermoplastic polymers which are typically used to
23 form film layers in plastic packaging articles. In the manufacture of certain
24 packaging articles, well-known thermosets can also be used as a polymeric
25 diluent.

26 Selecting combinations of a diluent and the composition of the present
27 invention depends on the properties desired. Polymers which can be used as
28 the diluent include, but are not limited to, polyethylene, low or very low density

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1 polyethylene, polypropylene, polyvinyl chloride, and ethylene copolymers
2 such as ethylene-vinyl acetate, ethylene-alkyl acrylates or methacrylates,
3 ethylene-acrylic acid or methacrylic acid, and ethylene-arylic or metharylic
4 acid ionomers. In rigid packaging applications, polystyrene is often used.
5 Blends of different diluents may also be used. However, as indicated above,
6 the selection of the polymeric diluent largely depends on the article to be
7 manufactured and the end use. Such selection factors are well known in the
8 art.

9 If a diluent polymer such as a thermoplastic is employed, it should further be
10 selected according to its compatibility with the composition of the present
11 invention. In some instances, the clarity, cleanliness, effectiveness as an
12 oxygen-scavenger, barrier properties, mechanical properties and/or texture of
13 the article can be adversely affected by a blend containing a polymer which is
14 incompatible with the composition of the present invention.

15 A blend of a composition of the present invention with a compatible polymer
16 can be made by dry blending or by melt-blending the polymers together at a
17 temperature in the approximate range of 50°C to 250°C. Alternative methods
18 of blending include the use of a solvent followed by evaporation. When
19 making film layers or articles from oxygen-scavenging compositions, extrusion
20 or coextrusion, solvent casting, injection molding, stretch blow molding,
21 orientation, thermoforming, extrusion coating, coating and curing, lamination
22 or combinations thereof would typically follow the blending.

23 Layers comprising the composition of the present invention may be in several
24 forms. They may be in the form of stock films, including "oriented" or "heat
25 shrinkable" films, which may ultimately be processed as bags, etc., or in the
26 form of stretch-wrap films. The layers may also be in the form of sheet inserts
27 to be placed in a packaging cavity. In rigid articles such as beverage
28 containers, thermoformed trays or cups, the layer may be within the

1 container's walls. Even further, the layer may also be in the form of a liner
2 placed with or in the container's lid or cap. The layer may even be coated or
3 laminated onto any one of the articles mentioned above.

4 In multi-layered articles, the scavenging layer comprising the composition of
5 the present invention may be included with layers such as, but not necessarily
6 limited to, "oxygen barriers", i.e., layers of material having an oxygen
7 transmission rate equal to or less than 100 cubic centimeters-mil per square
8 meter (cc-mil/m²) per day per atmosphere pressure at room temperature, i.e.,
9 about 25°C. Typical oxygen barriers comprise poly(ethylene vinyl alcohol),
10 polyacrylonitrile, polyvinyl chloride, poly(vinylidene dichloride), polyethylene
11 terephthalate, silica and polyamides. Metal foil layers can also be employed.

12 Other additional layers may include one or more layers which are permeable
13 to oxygen. In one preferred packaging construction, especially for flexible
14 packaging for food, the layers include, in order starting from the outside of the
15 package to the innermost layer of the package, (i) an oxygen barrier layer,
16 (ii) a scavenging layer, i.e., the scavenging composition as defined earlier,
17 and, optionally, (iii) an oxygen permeable layer. Control of the oxygen barrier
18 property of (i) allows a means to regulate the scavenging life of the package
19 by limiting the rate of oxygen entry to the scavenging composition (ii), and
20 thus limiting the rate of consumption of scavenging capacity. Control of the
21 oxygen permeability of layer (iii) allows a means to set an upper limit on the
22 rate of oxygen scavenging for the overall structure independent of the
23 composition of the scavenging composition (ii). This can serve the purpose of
24 extending the handling lifetime of the films in the presence of air prior to
25 sealing of the package. Furthermore, layer (iii) can provide a barrier to
26 migration of the individual components in the scavenging films or by-products
27 of scavenging into the package interior. Even further, layer (iii) also improves
28 the heat-sealability, clarity and/or resistance to blocking of the multi-layer film.

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- 1 Further, additional layers such as adhesive layers may also be used.
2 Compositions typically used for adhesive layers include anhydride functional
3 polyolefins and other well-known adhesive layers.
- 4 To determine the oxygen scavenging capabilities of a composition, the rate of
5 oxygen scavenging can be calculated by measuring the time that elapsed
6 before the article depletes a certain amount of oxygen from a sealed
7 container. For instance, a film comprising the scavenging component can be
8 placed in an air-tight, sealed container of a certain oxygen containing
9 atmosphere, e.g., air which typically contains 20.9% oxygen by volume.
10 Then, over a period of time, samples of the atmosphere inside the container
11 are removed to determine the percentage of oxygen remaining. The
12 scavenging rates of the composition and layers of the present invention will
13 change with changing temperature and atmospheric conditions.
- 14 When an active oxygen barrier is prepared, the scavenging rate can be as
15 low as 0.1 cc oxygen per gram of composition of the present invention per
16 day in air at 25°C and a 1 atmosphere pressure. However, preferable
17 compositions of this invention have rates equal to or greater than 1 cc oxygen
18 per gram per day, thus making them suitable for scavenging oxygen from
19 within a package, as well as suitable for active oxygen barrier applications.
20 Many compositions are even capable of more preferable rates equal to or
21 greater than 5.0 cc O₂ per gram per day.
- 22 Generally, film layers suitable for use as an active oxygen barrier can have an
23 oxygen transmission rate as high as 10 cc oxygen per square meter per mil
24 per day when measured in air at 25°C and 1 atmosphere pressure.
25 Preferably, a layer of this invention has an oxygen transmission rate less than
26 about 1 cc oxygen per square meter per mil per day, and more preferably has
27 an oxygen transmission rate less than about 0.2 cc oxygen per square meter
28 per rail per day under the same conditions, thus making it suitable for active

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1 oxygen barrier applications as well as for scavenging oxygen from within a
2 package.

3 In an active oxygen barrier application, it is preferable that the combination of
4 oxygen barriers and any oxygen scavenging activity create an overall oxygen
5 transmission rate of less than about 1.0 cubic centimeter-mil per square
6 meter per day per atmosphere pressure at 25°C. Another definition of
7 acceptable oxygen scavenging is derived from testing actual packages. In
8 actual use, the scavenging rate requirement will largely depend on the
9 internal atmosphere of the package, the contents of the package and the
10 temperature at which it is stored.

11 In a packaging article made according to this invention, the scavenging rate
12 will depend primarily on the amount and nature of the composition of the
13 present invention in the article, and secondarily on the amount and nature of
14 other additives (e.g., diluent polymer, antioxidant, etc.) which are present in
15 the scavenging component, as well as the overall manner in which the
16 package is fabricated, e.g., surface area/volume ratio.

17 The oxygen scavenging capacity of an article comprising the invention can be
18 measured by determining the amount of oxygen consumed until the article
19 becomes ineffective as a scavenger. The scavenging capacity of the
20 package will depend primarily on the amount and nature of the scavenging
21 moieties present in the article, as discussed above.

22 In actual use, the oxygen scavenging capacity requirement of the article will
23 largely depend on three parameters of each application:

24 (1) the quantity of oxygen initially present in the package;

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1 (2) the rate of oxygen entry into the package in the absence of the
2 scavenging property; and

3 (3) the intended shelf life for the package.

4 The scavenging capacity of the composition can be as low as 1 cc oxygen per
5 gram, but is preferably at least 10 cc oxygen per gram, and more preferably
6 at least 50 cc oxygen per gram. When such compositions are in a layer, the
7 layer will preferably have an oxygen capacity of at least 250 cc oxygen per
8 square meter per mil thickness and more preferably at least 500 cc oxygen
9 per square meter per mil thickness.

10 Other factors may also affect oxygen scavenging and should be considered
11 when selecting compositions. These factors include but are not limited to
12 temperature, relative humidity, and the atmospheric environment in the
13 package.

14 Applicants have achieved a composition for a rigid beverage and food
15 container comprising PET and/or PEN, the container incorporating an oxygen
16 scavenging component of cyclic olefin which oxidizes oxygen in the interior of
17 the container without giving off odor and/or taste as a result of its oxygen
18 scavenging function, nor does it cause a change in molecular weight. This is
19 because the cyclic olefin oxygen scavenging component does not fragment
20 as it oxidizes, Thus the composition maintains the structural integrity of the
21 container while avoiding the problem of imparting oxidation byproducts to the
22 packaged material.

23

24 EXAMPLES

25 Objects and advantages of this invention are further illustrated by the
26 following examples. The particular materials and amounts thereof, as well as

1 other conditions and details, recited in these examples should not be used to
2 unduly limit this invention.

3

4 Example 1

5 Preferred embodiments of the present invention include polymers and
6 oligomers, which contain cyclohexene groups accessible to free oxygen
7 molecules. These polymers or oligomers may be prepared from any of a
8 number of methods though one preferred reaction comprises 1, 2, 3, 6,
9 tetrahydrophthalic anhydride. This anhydride is a low cost monomer derived
10 from butadiene, which makes it particularly attractive on a commercial scale.
11 The anhydride may be used to make polyester resins such as by reaction with
12 diols. It may also be reacted with hydroxy or polyhydroxy compounds to
13 produce half esters suitable for subsequent use in plastic film and materials
14 manufacture.

15

16 Example 2

17 Non-aromatic alkenyl benzyl alcohols (e.g. tetrahydrobenzyl alcohols) may
18 also be reacted with certain compounds to produce useful scavengers. For
19 instance tetrahydrobenzyl alcohol may be reacted with compounds containing
20 a carboxylic acid, acid halide, ester, anhydride and/or isocyanate functionality.
21 These compounds may be small molecules or oligomers or polymers. For
22 example, tetrahydrobenzyl alcohol may be reacted with styrene, maleic
23 anhydride copolymers or with polyfunctional isocyanates.

24

25 Example 3

26 Cyclohexene dimethanol compounds may be used to prepare oxygen
27 absorbing polyesters and polyurethanes.

28

29 Example 4

1 As another example, tetrahydrobenzoic acid and tetrahydrobenzaldehyde
2 may also be used to modify various hydroxyl functional materials.

3

4 Example 5

5 Reactions such as the functionalization of polymers may be carried out by a
6 reactive extrusion process. For instance this may be a transesterification
7 process.

8

9 Example 6

10 Cyclohexene anhydride may be used in the preparation of useful oxygen
11 scavengers. These cyclohexene anhydrides may be prepared by from a
12 diene monomer such as butadiene with maleic anhydride. Of commercial
13 attractiveness are their low cost and their ability to be converted into a
14 number of useful intermediates. In addition, they may also be used to
15 functionalize OH containing polymers. The half esters, which form rapidly
16 when a cyclic anhydride reacts with an OH group, may be subsequently
17 neutralized and the resultant materials dispersed in ionomers or ethylene
18 acrylic acid copolymers (for instance).

19

20 For ease of use, small functionalized molecules such as the reaction product
21 of four moles of tetrahydrophthalic anhydride with pentaerythritol may be
22 prepared either by heating in a mutual solvent or by a reactive extrusion
23 process. These may then be dispersed into a commodity polymer such as
24 EVA.

25

26 The cyclohexene anhydrides may also be converted into linear polyesters by
27 reaction with ethylene glycol and the like.

28

29 Example 7

1 Useful anhydrides are cyclic anhydrides and in particular the Diels Alder
2 adducts of various alkenes. Typically this will comprise 1, 3 butadiene (and
3 substituted derivatives) with other compounds able to complete a Diels Alder
4 type reaction. The resulting anhydrides may then be used in the manufacture
5 of various oxygen scavengers, and polymers containing same.

6
7 Example 8

8 Film structures, coatings, and molded articles, as well as sachets and
9 impregnated matrices, are envisaged incorporating oxygen scavengers as
10 discussed previously. Also included are transition metal catalysts such as
11 used in the prior art for catalyzing oxygen scavenging reactions. Optionally
12 initiators or triggers for the reaction may also be included.

13
14 Example 9

15
16 Preparation of a low molecular weight oxidizable oil from 3-Cyclohexene-1-
17 carbonyl chloride and triethylene glycol.

18
19 3-Cyclohexene-1-carbonyl chloride was prepared as follows:

20
21 50g of thionyl chloride was added to 27.6g of 3-cyclohexene-1-carboxylic acid
22 and the solution was stirred for two hours at 50°C. Excess thionyl chloride
23 was removed under vacuum and the resulting yellow brown oil was purified
24 by distillation under vacuum (bp 80-82°C at 18-19mm Hg).

25
26 The oil was then prepared in the following manner:

27
28 In a 250 ml flask fitted with a drying tube was placed 18.7g of 3-cyclohexene-
29 1-carbonyl chloride and 40cc of methylene chloride. A solution of 9.6g of
30 triethylene glycol in 20ml of methylene chloride was added and the reaction

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1 was stirred for 2 hours at room temperature, by which time the evolution of
2 hydrochloric acid had ceased.

3

4 80ml of 10% aqueous sodium bicarbonate was added to the reaction mixture
5 and the mixture was vigorously stirred for 45 minutes. The organic layer was
6 collected, washed with water and then dried with magnesium sulphate. The
7 methylene chloride was removed under reduced pressure giving a colorless
8 oil.

9 The cyclohexene oil was compounded into a film with the following parts by
10 weight:

11

| | |
|---|------|
| 12 Oil | 12 |
| 13 Silica | 5 |
| 14 Benzophenone | 0.3 |
| 15 Cobalt (111) acetylacetonate | 0.28 |
| 16 Ethylene vinyl acetate copolymer (18% EVA) | 90 |

17

18 A similar film was prepared using sunflower seed oil in place of the
19 cyclohexene based oil.

20

21 Both films were exposed to 4 minutes of UV light, then sealed in oxygen
22 barrier bags and stored in the dark.

23

24 Both materials scavenged oxygen after photoexposure and the sunflower oil
25 based material was a faster scavenger than the cyclohexene oil based
26 material. However, gas chromatography of the headspace of the bags post
27 oxidation revealed that there was a very large difference in the levels of
28 volatile components. The cyclohexene based material produced less than
29 3% of the volatile components produced by the sunflower oil based material.

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1

2 The cyclohexene based films were stable for more than 300 days if stored at
3 room temperature in the absence of light (i.e., the oxygen concentration in a
4 sealed package containing the film specimens was essentially unchanged
5 after storage for this time period).

6

7 A similar cyclohexene based film was prepared, this time using 3,4 dimethyl-
8 3-cyclohexene-1-carbonyl chloride as the starting material. This film was a
9 much faster oxygen absorber than the film prepared from the unsubstituted
10 product. The film from the substituted produced less than 10% of the total
11 volatile components produced from an equivalent film made from sunflower
12 oil.

13

14 The dimethyl cyclohexene based films were stable for at least two hundred
15 days when stored at room temperature in the absence of light. The stability of
16 similar vegetable oil based films was limited to around 50 days.

17

18 This series of experiments revealed the following:

19

- 20 1. Cyclohexene functionalized materials are effective oxygen absorbers.
- 21 2. The speed of reaction may be increased by substituting methyl groups
22 adjacent to the double bond.
- 23 3. Cyclic alkene based materials produce much lower levels of volatile
24 oxidation products than linear alkene based materials.
- 25 4. The storage stability of cyclohexene containing films is excellent.

26

27 Example 10

28 Preparation of an oxidizable polyester resin.

29

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1 In a three neck round bottom flask equipped with a Dean and Stark trap,
2 reflux condenser and nitrogen inlet/exit were placed the following materials:

3

4 cis-1,2,3,6-Tetrahydrophthalic anhydride 35.54g

5 1,4-Butanediol 20g

6

7 75ml of xylene was added, so that the trap was full of xylene and the mixture
8 was brought to reflux. The reaction was refluxed for six and a half hours:
9 0.55g of p-Toluenesulfonic acid monohydrate was added and reflux was
10 continued for a further six and a half hours.

11 25ml of xylene was removed from the trap and the mixture was refluxed for a
12 further one hour. A very viscous pale colored solution was obtained.

13

14 The solution was extracted with methanol to remove the acid catalyst, and
15 was diluted with dichloromethane prior to use.

16

17 The polymer was obtained as a 38% w/w solids solution in
18 toluene/dichloromethane. To 12.37 g of the polymer solution was taken
19 0.0213 g cobalt Ten-Cem® (OMG Inc.) in 5 mL of dichloromethane and
20 0.0069 g of Quantacure™CPTX (1-chloro-4-propoxy-thioxanthone, Great
21 Lakes Fine Chemicals) was added. The mixture was stirred for a few minutes
22 and a film was cast onto the surface of the another film at a wet thickness of
23 about 1 mm. A second film was formulated as follows and cast as above:
24 12.64 g polymer solution, 0.0318 g cobalt Ten-Cem® and 0.0074 g
25 4,4'-dimethoxybenzophenone (DMOBP, Spectrum Quality Products Inc.).

26

27 The dried films were irradiated for 2.5 minutes with a combination of
28 germicidal and backlight UV lamps. The approximate dose of UVC was
29 1350mJcm² and the approximate dose of UVA was 1950mJcm². The

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- 1 irradiated films were sealed in a barrier pouch along with 120cc of air. The
2 oxygen content was monitored with time and the following results were
3 obtained:

| Film #1, 4.7g, 1020 ppm Cobalt and 1470 ppm CPTX | |
|--|----------------|
| Elapsed Time (days) | Percent Oxygen |
| 0 | 20.6 |
| 1 | 19.2 |
| 2 | 18.4 |
| 3 | 16.9 |

4

| Film #2, 4.8g, 1500 ppm Cobalt and 1480 ppm DMOBP | |
|---|----------------|
| Elapsed Time (days) | Percent Oxygen |
| 0 | 20.6 |
| 1 | 19.3 |
| 2 | 18.6 |
| 3 | 17.0 |

5

- 6 This example illustrates that polyesters derived from tetrahydrophthalic
7 anhydride are useful oxygen scavengers.

8

9 Example 11

- 10 Preparation of an oxidizable polymer from 3-Cyclohexene-1-methanol and an
11 alternating copolymer of maleic anhydride and octadecene.

12

- 13 In a three neck round bottom flask equipped with condenser and nitrogen
14 inlet was placed 20 g of poly(maleic anhydride-alt-1-octadecene). 80 cc of
15 methylene chloride was added and the mixture was stirred to dissolve. After

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1 a clear solution had been obtained 3.2g of 3-Cyclohexene-1-methanol was
2 added, and washed into the flask with a further 10cc of methylene chloride.

3

4 The mixture was refluxed with stirring under nitrogen for two hours, then left
5 overnight at room temperature. The solution was refluxed for a further three
6 hours and allowed to cool to room temperature.

7

8 The polymer was obtained as a 21.9 wt. % solution in dichloromethane. To
9 20.51 g of the polymer solution was added 0.0201 g of cobalt Ten-Cem®
10 (OMG Inc., 22.5% Co by wt.) dissolved in 5 mL of toluene solution and
11 0.0038 g of Quantacure™ BMS (4-benzoyl-4'-methyl(diphenyl sulfide)
12 available from Great Lakes Fine Chemicals Ltd.). The mixture was stirred for
13 a few minutes and a film was cast using a draw down bar to a wet film
14 thickness of about 1 mm.

15

16 A second film was formulated as follows: 20.10 g polymer solution, 0.0474 g
17 cobalt Ten-Cem®, 0.0079 g 4,4'-dimethylbenzophenone (DMBP, from
18 Lancaster Synthesis). A third film was formulated as follows: 20.84 g
19 polymer solution, 0.0398 g cobalt Ten-Cem®, 0.0085 g
20 2-isopropylthioxanthone (ITX, First Chemical Co.).

21

22 The dried films were irradiated for 2.5 minutes with a combination of
23 germicidal and backlight UV lamps. The approximate dose of UVC was
24 1350 mJ/cm² and the approximate dose of UVA was 1950 mJ/cm². The
25 irradiated films were sealed in a barrier pouch along with about 120 cc of air.
26 The oxygen content was monitored with time as described elsewhere. The
27 following results were obtained:

28

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| Film Sample #1, 1.34g, with 1004 ppm Cobalt and 844 ppm BMS | |
|---|----------------|
| Elapsed Time (days) | Percent Oxygen |
| 0 | 20.6 |
| 1 | 12.2 |
| 2 | 7.5 |
| 5 | 6.2 |

1

| Film Sample #2, 3.04g, with 2420 ppm Cobalt and 1795 ppm DMBP | |
|---|----------------|
| Elapsed Time (days) | Percent Oxygen |
| 0 | 20.6 |
| 1 | 11.8 |
| 2 | 10.0 |
| 5 | 9.7 |

2

3

| Film Sample #3, 2.09g, with 1960 ppm Cobalt and 1860 ppm ITX | |
|--|----------------|
| Elapsed Time (days) | Percent Oxygen |
| 0 | 20.6 |
| 1 | 13.8 |
| 2 | 10.5 |
| 5 | 10.0 |

4

5 The results suggest that the reaction of a polymeric anhydride and
6 tetrahydrobenzyl alcohol is a useful route to oxygen scavenging plastics.

7

8 Example 12

9 Preparation of a Cyclohexene containing polymer by transesterification

10

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1 To a 2L resin kettle was taken 180 g of polyethylene-co-methyl acrylate
2 (EMAC® SP2260, Chevron, 24 wt. % methyl acrylate) and 1 L of toluene.
3 The kettle was equipped with a mechanical overhead stirrer, Dean-Stark trap
4 and a condenser. The kettle was heated to melt the polymer. To the stirred
5 solution was added 28.12 g of 3-cyclohexene-1-methanol, followed by the
6 addition of 2.145 g of 4-(2-hydroxyethoxy)benzophenone. (Note: this
7 benzophenone derivative was prepared by the method of Yoshino et al. *Bull.*
8 *Chem Soc. Japan*, 1973, 46, 553-6 using 4-hydroxybenzophenone, ethylene
9 carbonate and tetraethylammonium iodide.) The catalyst, titanium (IV)
10 isopropoxide (1.05g) was added. The mixture turned yellow and the reflux
11 rate increased. Heat was maintained for 4 hours and about 75 mL of
12 condensate was removed in four fractions. An additional 0.5 g of titanium
13 isopropoxide was added and heat was maintained for an additional 8 hours.
14 Additional toluene was added as needed to maintain the reaction volume.
15 Again an additional 0.5 g of catalyst was added and heat maintained for
16 another 8 hours. Analysis of the condensate showed no more production of
17 methanol. The reaction mixture was cooled to a gel and precipitated into
18 methanol. The polymer was washed with methanol until nothing was
19 extracted into the methanol fractions.
20
21 The above resin containing cyclohexene pendant groups and a covalently
22 bound benzophenone derivative was melt compounded with 500 ppm
23 vitamin E as the antioxidant and 10% of an EVA based cobalt (II) oleate
24 (Shepherd Chemicals) masterbatch. The masterbatch contained 1.0% cobalt
25 metal by weight. Samples were compression molded and cut to 197.56 cm²
26 of UVC light (254 nm) and was sealed in an oxygen barrier pouch (Cryovac
27 P640B) with 300 cc of air and was stored in the dark at room temperature.
28 Headspace oxygen levels were monitored periodically by withdrawing a 4 cc
29 sample and analyzing using a Mocon model LC 700F oxygen analyzer. The
30 following results were obtained for the 1.9 g (7.8 mil thick) sample.

1

| Elapsed Time (days) | Percent Oxygen |
|---------------------|----------------|
| 0 | 20.6 |
| 1 | 15.6 |
| 5 | 5.0 |
| 14 | 2.1 |
| 21 | 1.2 |

2

3 This example illustrates excellent oxygen scavenging ability from this type of
4 polymer and the usefulness of a covalently bound photoinitiator.

5

6 Example 13

7 Preparation of oxidizable polyurethanes.

8

9 In a two necked 250ml flask equipped with reflux condenser and nitrogen
10 inlet/exit were placed the following materials:

11

| | |
|--------------------------------|-------|
| 12 1,6-Diisocyanatohexane | 6.5g |
| 13 3-Cyclohexene-1,1dimethanol | 5.23g |
| 14 2-Butanone | 70ml |

15

16 One drop of dibutyltin dilaurate was added and the mixture was stirred under
17 nitrogen for thirty minutes at room temperature. The mixture was then
18 brought to reflux for a further four hours and one drop of water in 10ml of
19 MEK was added. The mixture was refluxed for a further hour and then
20 allowed to cool to room temperature.

21

22 A polyurethane containing cyclic unsaturation was prepared from 1,6-
23 diisocyanatohexane and 3-cyclohexene-1,1-dimethanol. The polymer
24 (3.912 g) was taken into 10 mL dichloromethane and a solution of 0.0243 g of

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1 cobalt Ten-Cem® (OMG Inc.) in 5 mL of dichloromethane was added. To the
2 stirred mixture was added 0.0084 g of 4,4'-dimethylbenzophenone (DMBP,
3 Lancaster Synthesis). The mixture was stirred for about 15 minutes. A film
4 was cast from the solution on the surface of another film at a wet thickness of
5 about 1 mm. The dried film was triggered and tested as described in
6 example 3 above.

7

| 3.9g, with 1400 ppm Cobalt and 2150 ppm DMBP | |
|--|----------------|
| Elapsed Time (days) | Percent Oxygen |
| 0 | 20.6 |
| 1 | 18.3 |
| 4 | 13.1 |
| 5 | 9.5 |

8

9 These results suggest that polyurethanes derived from 3-Cyclohexene-1,1-
10 dimethanol are useful oxygen absorbers. These materials and alternative
11 formulations may be useful in formulating oxygen scavenging adhesive resins
12 for use in flexible packaging i.e., for use in lamination.

13

14 Example 14

15 Preparation of a poly (vinyl acetal) from poly(vinyl alcohol) and
16 3-Cyclohexene-1-carboxaldehyde.

17

18 In a 500ml flask equipped with nitrogen inlet/exit and mechanical stirrer was
19 placed 150 ml of a 70/30 mix of dioxane/ethanol and 10g of poly(vinylalcohol).
20 The mixture was stirred and 15.7g of 3-Cyclohexene-1-carboxaldehyde was
21 added, followed by 0.25ml conc. HCl and 5 mg of hydroquinone. The mixture
22 was refluxed for four hours, during which time the poly(vinyl alcohol) dissolved
23 and turned a pale yellow color, 0.5g of sodium acetate was added followed by

-91-

1 2.5g of urea, both in aqueous solution. The polymer precipitated and was
2 purified by addition of further dioxane then precipitation into water. The dried
3 polymer was found to contain approximately 63mole% of acetal groups.

4

5 A similar polymer was prepared from 3,4-dimethyl-3-cyclohexene-1-
6 carboxaldehyde and poly(vinyl alcohol) which contained approximately
7 65 mole% of acetal groups.

8

9 A solution of cobalt (III) acetylacetonate (20mg) and benzophenone (20mg)
10 in methylene chloride was added with stirring to a solution (1g) of each acetal
11 resin dissolved in 15ml of warm dioxane. The solution was poured into a
12 150mm diameter flat bottom petri dish and the solvent was allowed to
13 evaporate. The resultant film was held under high vacuum for 2-3 hours to
14 remove any residual solvent. A further sample containing 30% of a dibutyl
15 phthalate plasticiser was also prepared using the dimethyl substituted acetal
16 resin described above.

17

18 The film samples were exposed to 4 minutes of UVA radiation and then
19 vacuum packed in a barrier bag. 200ml of air was injected into the bag and
20 the puncture point was isolated by heat sealing. The pouch was stored in the
21 absence of light.

22

23 The following results were obtained for the unsubstituted resin:

24

| Elapsed Time (days) | Percent Oxygen |
|---------------------|----------------|
| 0 | 20.6 |
| 1 | no reading |
| 3 | 9.9 |
| 6 | 7.2 |

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| | |
|----|-----|
| 12 | 1.2 |
|----|-----|

1

2 The following results were obtained for the disubstituted resin:

| Elapsed Time (days) | Percent Oxygen |
|---------------------|----------------|
| 0 | 20.6 |
| 1 | 10.2 |
| 3 | 4.3 |
| 6 | 1.4 |
| 21 | 0 |

3

4 The following results were obtained from the plasticised resin:

5

| Elapsed Time (days) | Percent Oxygen |
|---------------------|----------------|
| 0 | 20.6 |
| 3 | 3.7 |
| 4 | 1.8 |
| 7 | 0.2 |
| 12 | 0 |

6

7 These results demonstrate the following principles:

8

9 1. Cyclohexene based acetal resins are effective oxygen scavengers.

10

11 2. The substituted cyclohexene rings provide faster oxygen scavengers than
12 the unsubstituted resins.

13

14 3. A plasticiser tends to increase the rate of oxygen scavenging.

1
2
3
4 Non-limiting examples are given in Examples 15 and 16 below of
5 experimental conditions that were used for preparation of the polymers.
6 Non-limiting examples of the resin preparation followed by steam stripping as
7 well as compounding the polymers with oxidation catalyst, such as cobalt
8 oleate and a photoinitiator, such as Methanone,
9 [5'-(5'-(4-benzoylphenyl)[1,1':3', 1"-terphenyl]-4,4"-diyl]bis[phenyl- (hereinafter
10 referred to as BBP³), and extruded into a 3-layer film having a PE/oxygen
11 scavenging polymer/PE structure are provided in Examples 17 through 20
12 below.

13 Headspace studies of three layer films made by compounding catalyst
14 package with both fresh and aged (20 months stored in air at ambient
15 temperature) resins after UV triggering give a very fast rate of oxygen
16 scavenging and the resulting packages are relatively non-odorous.
17 Non-limiting examples of such studies are given in Examples 21 and 22.
18 Furthermore, the above polymer can be further diluted by a lower cost oxygen
19 permeable resin, such as EBAC or PE or EVA, down to 50 and even 25% of
20 the original concentration and still maintain a high oxygen scavenging rate, as
21 the non-limiting examples in Examples 23 and 24 show.

22
23 Example 15

24 Polymer Preparation (C1641-6)

25 550 ml of decalin® was placed in a flask. To this was added 350 g of
26 Chevron EMAC SP-2260 which has 24 weight % of methyl acrylate
27 (0.9767 moles of methyl acrylate) and 0.48 g of Irganox®1076 (0.1 mole).
28 The temperature of the mixture was gradually raised while stirring. When the

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1 temperature reached approximately 120°C, 127.1 g (0.9767 moles) of
2 3-methyl-cyclohex-1-ene-4-methanol (97%) was added. When the
3 temperature reached approximately 140°C, 4.8 g of the catalyst $\text{Ti}(\text{OC}_2\text{H}_5)_4$
4 was added a portion at a time. The temperature was maintained at 170°C
5 while stirring. The course of the reaction was observed by subjecting
6 samples of the mixture to NMR at hourly intervals. The percent conversion is
7 given in Table 1 below. After 5 hours of reaction, the mixture was cooled and
8 400 ml of CHCl_3 was added and the mixture was then precipitated by adding
9 it to 4 liters of CH_3OH in a Waring blender. The precipitate is filtered and
10 washed with CH_3OH and dried in a vacuum oven at 50°C. The dried mixture
11 yielded 407.5 g of ethylene/methyl acrylate/methyl cyclohexene methyl
12 acrylate (EMCM).

13 Table 1

| Time (hours) | Percent Conversion |
|--------------|--------------------|
| 1 hour | 50% |
| 2 hours | 62.3% |
| 3 hours | 65.5% |
| 5 hours | 87.1% |

14
15 390 grams of a combination of the above prepared polymer and the same
16 polymer prepared under the same conditions in a different batch, which
17 together have a conversion percentage of 68.8%, was solvent coated with
18 3.25 g cobalt-neodecanoate in 70 ml normal hexane. The mixture was
19 tumble dried for 1.5 hours and residual solvent removed in a vacuum.

20

21 Example 16

22

Polymer Preparation

23 600 ml of decalin was placed in a flask. To this was added 334 grams of
24 Chevron SP-2260 (0.9330 moles of methyl acrylate) and 0.44 g of Irganox®

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1 1010 (0.1% mole). The temperature of the mixture was gradually raised while
2 stirring. When the temperature reached approximately 120°C, 104.6 g
3 (0.93 moles) of cyclohex-1-ene-4-methanol was added. When the
4 temperature reached approximately 140°C, 4.4 g of the catalyst $\text{Ti}(\text{OC}_2\text{H}_5)_4$
5 was added a portion at a time. The temperature was maintained at 160°C
6 while stirring. The course of the reaction was observed by subjecting
7 samples of the mixture to NMR at hourly intervals. The percent conversion is
8 given in Table 2 below. After 3 hours of reaction, the mixture was cooled and
9 400 ml of CHCl_3 was added and the mixture was then precipitated by adding
10 it to 4 liters of CH_3OH in a Waring blender. The precipitate was filtered and
11 washed with CH_3OH and dried in a vacuum oven at 50°C. The dried mixture
12 yielded 380.5 g of polymer.

13

Table 2

| Time (hours) | Percent Conversion |
|--------------|--------------------|
| 1 hour | 43.8% |
| 2 hours | 56.7% |
| 3 hours | 55.7% |

14

15 185 grams of the above-prepared polymer was combined with 45 ml normal
16 hexane and 1.54 g cobalt-neodecanoate resulting in 1000 ppm of cobalt ion
17 and 0.0185 g Irganox® 1010 resulting in 100 ppm Irganox®. The mixture
18 was heated and blended and then dried in a vacuum-oven. The resulting
19 compound was extruded into a film.

20 Additionally, 185 grams of the above-prepared polymer was combined with
21 45 ml normal hexane and 1.54 g cobalt-neodecanoate (resulting in 1000 ppm
22 of cobalt ion) and 0.046 g Irganox® 1010 (resulting in 250 ppm Irganox®).
23 The mixture is heated and blended and then dried in a vacuum-oven. The
24 resulting compound is extruded into a film.

1 Example 17

2 EMCM Made in ZSK-30 Extruder

3 Ethylene-methyl acrylate copolymer (EMAC) was fed into a Werner &
4 Pfleiderer ZSK-30 twin screw extruder at 6 kg/hr, and the reactants and
5 catalysts were added to the extruder in a subsequent reaction zone. The
6 catalyst $\text{Ti}(\text{OC}_3\text{H}_7)_4$ was added with the reactants at 3 mol % or at a rate of
7 148 cc/hr. Irganox®/Toluene solution was added at 4.5 g/900 cc using a
8 Milton Roy 29/290 mini-pump. To obtain 100 ppm of Irganox®, it must be
9 added at 2.2 cc/min. To obtain 50 ppm of Irganox, it must be added at
10 1.1 cc/min. Cyclohexane methyl alcohol with 1,000 ppm of an antioxidant of
11 BHT was added via a Milton Roy dual head at 1958 cc/hr. Steam is injected
12 into the system at 800 cc $\text{H}_2\text{O}/\text{Hr}$ at the end of the reaction zone.

13 51 lbs of EMCM product (100 ppm Irganox® 1010, 59.3% methyl alcohol
14 (MA), 2.98 g/10 min. Melt Flow) was produced over a period of approximately
15 2 hours.

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1 Example 182 EMCM Made in ZSK-30

3 45 lbs of EMCM product (100 ppm Irganox®1010, 2.38 g/10 min Melt Index)
4 was extruded over a period of approximately 3 hours. A dual steam stripping
5 setup was used in which pressurized injectors at zones 4 and 11 of the
6 extruder pumped steam at 1076 cc/hr and 728 cc/hr, respectively. Both
7 injectors were Pulse 680 pumps with a pressure of at least 800 psi, except at
8 the first measured time interval when injector (No. 4) was measured at
9 500-550 psi and injector (No. 11) was measured at 500 psi.

10 Example 1911 Co-polymerization of Styrene and 3-Cyclohexene-1-Methanol Methacrylate

12 In a 1-liter round bottom flask, 65 grams styrene (0.625 mole), 113 grams of
13 3-cyclohexene-1-methanol methacrylate (0.625 mole), 1.25 grams of Benzoyl
14 peroxide and 450 grams of toluene were mixed and degassed by freeze-thaw
15 cycles. The degassed solution was polymerized at 70-75°C for 48 hours and
16 discharged into 2 liters of methanol in a Waring Blender. The product isolated
17 was dried in a vacuum oven at 50°C for 2 hours to give 155 grams of
18 co-polymer. NMR analysis indicates it contains 48 mole % of styrene and
19 52 mole % of 3-cyclohexene-1-methanol methacrylate. Tg by DSC is 66°C.

20

21 Example 2022 Oxygen Scavenging Test of Styrene/CHMA Copolymer

23 90 weight % of the above-mentioned co-polymer and 10 weight % of a EVA
24 based Master batch containing 1 weight % of co-oleate and 1 weight % of a
25 photoinitiator (BBP³) were processed into a 8 mil thick monolayer film. A
26 100 cm² film was irradiated at both sides to receive 800 mJoules/cm² of

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1 254 nm UV on each side and sealed into a foil bag containing 300 cc of 1%
 2 oxygen. The oxygen uptake was monitored up to 11 days at 4°C and at room
 3 temperature. The results are shown in Tables 3 (4°C) and 4 (room
 4 temperature).

5 Table 3

| Time (days) | O ₂ Meas. Vol% | O ₂ Meas. Vol, ml | Vol—O ₂ Used ml | O ₂ Uptake ml/g | O ₂ Uptake Avg Rate cc/m ² /day | Instant Rate cc/m ² /day | O ₂ Capacity cc/m ² /mil |
|-------------|---------------------------|------------------------------|----------------------------|----------------------------|---|-------------------------------------|--|
| 0.0 | 1.05 | 3.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.1 | 0.94 | 2.77 | 0.32 | 0.18 | 14.79 | 14.79 | 1.62 |
| 3.9 | 0.49 | 1.42 | 1.63 | 0.92 | 20.73 | 23.03 | 8.15 |
| 4.8 | 0.39 | 1.11 | 1.91 | 1.08 | 19.81 | 15.78 | 9.57 |
| 7.0 | 0.30 | 0.84 | 2.17 | 1.22 | 15.40 | 5.72 | 10.83 |
| 11.0 | 0.09 | 0.25 | 2.74 | 1.54 | 12.43 | 7.22 | 13.72 |

7 Table 4

| Time (days) | O ₂ Meas. Vol% | O ₂ Meas. Vol, ml | Vol—O ₂ Used ml | O ₂ Uptake ml/g | O ₂ Uptake Avg Rate cc/m ² /day | Instant Rate cc/m ² /day | O ₂ Capacity cc/m ² /mil |
|-------------|---------------------------|------------------------------|----------------------------|----------------------------|---|-------------------------------------|--|
| 0.0 | 1.04 | 3.12 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.1 | 0.48 | 1.42 | 1.65 | 1.03 | 75.28 | 75.28 | 8.26 |
| 3.9 | 0.09 | 0.26 | 2.78 | 1.73 | 35.40 | 19.96 | 13.92 |
| 4.8 | 0.04 | 0.11 | 2.93 | 1.82 | 30.26 | 7.89 | 14.63 |
| 7.0 | 0.01 | 0.03 | 3.01 | 1.87 | 21.39 | 1.91 | 15.05 |
| 11.0 | 0.01 | 0.03 | 3.01 | 1.87 | 13.64 | 0.00 | 15.05 |

9 Example 21

10 Polymerization of 3-cyclohexene-1-methanol acrylate

1 75 grams (0.45 mole) of 3-cyclohexene-1-methanol acrylate (CHAA), 200 ml
2 of toluene and 0.5 grams of Benzoyl peroxide were charged into a 500 ml
3 round-bottomed flask and degassed by freeze-thaw cycles. The degassed
4 solution was polymerized at 70-75°C for 48 hours. The viscous polymer
5 solution was worked up by precipitating in methanol solution in a Waring
6 blender. After vacuum drying at room temperature for 3 days, the product is a
7 rubbery clear polymer which weighs 53 grams.

8

9 Example 22

10 Headspace Analysis of O₂ Scavenging in
11 Dowlex® 3010/EMCM/Dowlex® 3010 Films

12 Oxygen scavenging analysis was performed using a Mocon HS750 with a
13 headspace volume of 300 cc. The sample tested was a 0.48 g three-layer
14 film with Dowlex® 3010 film for the two outside layers and steam stripped
15 EMCM (59% converted) for the middle layer (50 ppm Irganox® 1010). The
16 thickness of the layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging
17 portion of the middle layer comprised 1000 ppm Cobalt salt, 1000 ppm BBP³
18 and was exposed for 1.6 minutes to 254 nm UV at 1 inch to receive
19 800 mJ/cm². The oxygen scavenging was tested with 300 cc 1% O₂ at 4°C.
20 The results of the tests are given below in Table 5. These results are plotted
21 along with the results of Example 20 in Figure 2, which graphically plots %
22 oxygen in headspace against time (days). The oxygen scavenging uptake
23 capacity is based on the total weight of the three-layer film.

1

Table 5

| Time (days) | O ₂ Meas. Vol% | O ₂ Meas. Vol, ml | Vol—O ₂ Used ml | O ₂ Uptake ml/g | O ₂ Uptake Avg Rate cc/m ² /day | Instant Rate cc/ m ² /day | O ₂ Capacity cc/m ² /mil |
|--------------------|------------------------------|------------------------------------|-------------------------------|----------------------------------|---|--|--|
| 0.0 | 1.04 | 3.12 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.8 | 0.74 | 2.18 | 0.89 | 1.84 | 57.93 | 57.93 | 44.25 |
| 1.9 | 0.46 | 1.33 | 1.70 | 3.54 | 45.85 | 37.36 | 84.85 |
| 3.0 | 0.29 | 0.83 | 2.18 | 4.54 | 36.87 | 21.87 | 109.08 |
| 5.8 | 0.14 | 0.39 | 2.60 | 5.42 | 22.46 | 7.41 | 130.08 |
| 7.8 | 0.09 | 0.25 | 2.74 | 5.71 | 17.67 | 3.51 | 136.95 |

2

3 Example 23

4

Headspace Analysis of O₂ Scavenging in

5

Dowlex® 3010/EMCM/Dowlex® 3010 Films

6 Oxygen scavenging analysis was performed using a Mocon HS750 with a
7 headspace volume of 300 cc. The sample tested was a 0.47 g three-layer
8 film with Dowlex® 3010 film for the two outside layers and steam stripped
9 EMCM for the middle layer (50 ppm Irganox 1010)). The thickness of the
10 layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle
11 layer comprised 1000 ppm Cobalt salt, 1000 ppm BBP³ (a photoinitiator)
12 exposed for 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm². The
13 oxygen scavenging was tested with 300 cc 1% O₂ at 4°C. These results are
14 plotted along with the results of Example 21 in Figure 2, which graphically
15 plots % oxygen in headspace against time (days).

1 Example 242 Headspace Analysis of O₂ Scavenging in Dowlex® 3010/3 EBAC:EMCM/Dowlex® 3010 Films

4 Oxygen scavenging analysis was performed using a Mocon HS750 with a
5 headspace volume of 300 cc. The sample tested was a 0.45 g three-layer
6 film with Dowlex® 3010 film for the two outside layers and 3:1 EBAC
7 (ethylene/butyl acrylate copolymer):EMCM (ethylene/methyl acrylate/
8 cyclohexenyl methyl acrylate) for the middle layer (50 ppm Irganox® 1010)).
9 The thickness of the layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging
10 portion of the middle layer comprised 1000 ppm of Cobalt salt, 1000 ppm
11 BBP³ was exposed for 1.6 minutes to 254 nm UV at 1 inch to receive
12 800 mJ/cm². The oxygen scavenging was tested with 300 cc 1% O₂ at 4°C.
13 These results are plotted along with the results of Example 22 in Figure 3,
14 which graphically plots % oxygen in headspace against time (days).

15

16 Example 2517 Headspace Analysis of O₂ Scavenging in Dowlex® 3010/18 EBAC:EMCM/Dowlex® 3010 Films

19 Oxygen scavenging analysis was performed using a Mocon HS750 with a
20 headspace volume of 300 cc. The sample tested was a 0.47 g three-layer
21 film with Dowlex® 3010 film for the two outside layers and 1:1 EBAC:EMCM
22 for the middle layer (50 ppm Irganox®1010)). The thickness of the layers
23 was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle layer
24 comprised 1000 ppm Cobalt Oleate salt, 1000 ppm BBP³ exposed for
25 1.6 minutes at 254 nm UV at 1 inch to receive 800 mJ/cm². The oxygen
26 scavenging was tested with 300 cc 1% O₂ at 4°C. The results of the tests are
27 given below in Table 6. These results are plotted along with the results of
28 Example 23 in Figure 3, which graphically plots % oxygen in headspace

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1 against time (days). The oxygen scavenging uptake capacity is based on the
2 total weight of the 3-layer film.

3 Table 6

| Time (days) | Head- space O ₂ (Vol%) | Head- space O ₂ (Vol, ml) | Vol—O ₂ Used (ml) | O ₂ Uptake (ml/g) | O ₂ Uptake Avg Rate (cc/m ² ·day) | Instant Rate (cc/m ² · day) | O ₂ Capacity cc/m ² |
|----------------|--|--|------------------------------------|------------------------------------|---|---|---|
| 0.0 | 1.09 | 3.27 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.8 | 0.74 | 2.18 | 1.03 | 2.20 | 63.00 | 63.00 | 51.63 |
| 1.8 | 0.50 | 1.45 | 1.73 | 3.68 | 48.52 | 36.18 | 86.43 |
| 4.8 | 0.17 | 0.48 | 2.67 | 5.8 | 27.73 | 15.51 | 133.45 |
| 6.1 | 0.12 | 0.34 | 2.81 | 5.98 | 23.17 | 5.60 | 140.45 |
| 6.9 | 0.10 | 0.28 | 2.86 | 6.09 | 20.84 | 3.40 | 143.20 |
| 7.9 | 0.08 | 0.22 | 2.92 | 6.21 | 18.46 | 2.62 | 145.90 |

4
5 Example 26

6 Headspace Analysis of O₂ Scavenging Capacity
7 in Dowlex® 3010/EMCM/Dowlex® 3010 Films

8 Oxygen scavenging analysis was performed using a Mocon HS750 with a
9 headspace volume of 300 cc. The sample tested was a 0.47 g three-layer
10 film with Dowlex® 3010 film for the two outside layers and steam stripped
11 EMCM for the middle layer (50 ppm Irganox®1010)). The thickness of the
12 layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle
13 layer comprised 1000 ppm Cobalt Oleate salt, 1000 ppm BBP³ exposed for
14 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm². The oxygen
15 scavenging was tested with 300 cc air at room temperature. The O₂ uptake
16 capacity is based on total weight of the 3-layer film. The results of the tests
17 are given below in Table 7. These results are plotted along with the results of
18 Example 26 in Figure 4, which graphically plots % oxygen in headspace
19 against time (days).

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Table 7

| Time (days) | Head-space O ₂ (Vol%) | O ₂ Vol, (ml) | Vol-O ₂ Used (ml) | O ₂ Uptake (ml/g) | O ₂ Uptake Avg Rate (cc/m ² ·day) | Instant Rate (cc/m ² ·day) | O ₂ Capacity (cc/m ²) |
|-------------|----------------------------------|--------------------------|------------------------------|------------------------------|---|---------------------------------------|--|
| 0.0 | 20.60 | 61.80 | 0.00 | 0.00 | 0.0 | 0.0 | 0.0 |
| 1.0 | 13.40 | 39.53 | 21.24 | 43.35 | 1058 | 1058 | 1062 |
| 2.0 | 12.20 | 35.38 | 24.72 | 50.45 | 616 | 173 | 1236 |
| 3.0 | 11.80 | 33.63 | 25.86 | 52.78 | 437 | 60 | 1293 |
| 6.2 | 11.80 | 33.04 | 25.86 | 52.78 | 207 | 0.0 | 1293 |

1

2 Example 27

3

Headspace Analysis of O₂ Scavenging Capacity in

4

Dowlex® 3010/EBAC:EMCM/Dowlex® 3010 Films

5 Oxygen scavenging analysis was performed using a Mocon HS750 with a
6 headspace volume of 300 cc. The sample tested was a 0.45 g three-layer
7 film with Dowlex® 3010 film for the two outside layers and 2:1 EBAC:EMCM
8 for the middle layer (50 ppm Irganox 1010)). The width of the layers was
9 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle layer
10 comprised 1000 ppm of Cobalt salts, 1000 ppm BBP³ exposed for
11 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm². The oxygen
12 scavenging was tested with 300 cc air at room temperature. The O₂ uptake
13 capacity is based on total weight of the 3-layer film. The results of the tests
14 are given below in Table 8. These results are plotted along with the results of
15 Example 23 in Figure 4, which graphically plots % oxygen in headspace
16 against time (days).

1

Table 8

| Time (days) | Head-space O ₂ (Vol%) | Head-space O ₂ Vol. (ml) | Vol-O ₂ Used (ml) | O ₂ Uptake (ml/g) | O ₂ Uptake Avg Rate (cc/m ² -day) | Instant Rate (cc/m ² -day) | O ₂ Capacity (cc/m ²) |
|-------------|----------------------------------|-------------------------------------|------------------------------|------------------------------|---|---------------------------------------|--|
| 0.0 | 20.60 | 61.80 | 0.00 | 0.00 | 0.0 | 0.0 | 0.0 |
| 1.0 | 17.70 | 52.21 | 8.56 | 18.20 | 426 | 426 | 428 |
| 2.0 | 17.40 | 50.46 | 9.43 | 20.05 | 235 | 43 | 471 |
| 3.0 | 17.10 | 48.74 | 10.28 | 21.87 | 174 | 45 | 514 |
| 6.2 | 17.10 | 47.88 | 10.28 | 21.87 | 83 | 0.0 | 514 |

2

3 Example 284 Taste Preference Test

5 The organoleptic quality of a film containing EMCM as the scavenging resin in
6 a multi-layer oxygen scavenging packaging structure was evaluated and
7 compared with an SBS (styrene/butadiene/styrene)-based oxygen
8 scavenging packaging structure. Films were triggered with 800 mJ/cm² of
9 254 nm UV. Packages containing ca. 200 ml of water were made and
10 vacuum/gas flushed to obtain a gas composition of 1% O₂:99% N₂. Packages
11 were stored at 40°F for seven days prior to taste testing. A forced preference
12 double blind Triangle taste test was carried out on water extracts of the
13 EMCM-based and SBS-based films.

14

15 Sensory results indicated that there was a significant difference (24 out of 28
16 respondents) between the EMCM-based and SBS-based structures. All 24
17 respondents who correctly identified the odd sample in the single test
18 preferred the taste of the water packaged in EMCM over SBS. As shown in
19 Table 9, Day 4 scavenging rates of the EMCM-based structures were lower
20 than the SBS counterpart. On Day 4, both structures had significant oxidation
21 and the obvious difference in flavor perception was attributed to the fewer and

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1 less objectionable by-products (fragments after oxidation of EMCM) of the
 2 EMCM oxygen scavenging system.
 3 In a second forced preference triangle taste test, water samples in
 4 EMCM-based scavenging structures were tested against water samples
 5 packaged in a standard barrier laminate film (R660B manufactured by
 6 Cryovac Division of Sealed Air Corporation). The packaged water extract
 7 samples were submitted to a sensory panel for forced preference double blind
 8 taste testing. Samples were tested after 8 days of scavenging. A significant
 9 difference in the taste was found between the samples packaged in the
 10 EMCM and the control packages. Surprisingly, the preference was towards
 11 the EMCM structure. Open comments stated that there was no off-flavor
 12 (normally associated with the SBS-based oxygen scavenging films) in the
 13 EMCM samples and that EMCM was "pretty close in taste to the control."
 14 Headspace oxygen levels reached by the EMCM structure were ca. 0.2%
 15 (down from 1%) at Day 8. Scavenging results of the EMCM film used during
 16 this test are also listed in Table 9.

17 Table 9
 18 Oxygen Scavenging
 19 Packaging Films

| Film Sample | Average Rate (cc/m ² -day) | Average Rate (cc/m ² -day) | Induction Period (days) | Peak Instantaneous Rate avg. (c) (cc/m ² -day) | Peak Instantaneous Rate (cc/m ² -day) |
|-----------------------------------|--|--|----------------------------|--|---|
| | Mean | St. dev. | | Mean | St. dev. |
| SBS Film | 51.0 ^a | 7.8 | <1 | 88.4 (1) | 14.1 |
| 1 st Sensory test EMCM | 41.6 ^a | 5.3 | <1 | 68.6 (2) | 11.4 |
| 2 nd Sensory Test EMCM | 30.5 ^b | 5.9 | <1 | 83.6 (2-3) | 19.4 |

20 ^aRate at 4 days.

21 ^bRate at 8 days.

22 ^cTime to reach peak rate in days.

1 Example 29

2 Taste Preference Test

3 Oxygen scavenging test films, 5 cm x 20 cm, were irradiated with 800 mJ/cm²
4 ultraviolet (254 nm) and heat tacked to the top of the test pouches (one per
5 pouch). The pouches (16 cm x 19 cm) were made from laminated barrier film
6 specifically designed to be oxygen impermeable. 21 gram slices of freshly
7 sliced turkey roll were put into sterilized 9 cm petri dishes (one per dish). The
8 dishes were, in turn, placed into the barrier pouches (one per pouch). The
9 pouches were heat sealed, filled with 300 cc 1% oxygen/99% nitrogen gas,
10 and stored at 4°C for the duration of the test.

11 Two types of oxygen scavenging polymers were compared in the test against
12 a control (barrier pouch alone, no oxygen scavenger). The oxygen
13 scavenging films were each three layer (ABA) structures in which the outer,
14 "A", layer was 0.5 mil thick LLDPE, and the middle, "B", layer was 1.0 mil thick
15 oxygen scavenging polymer (compounded with 1000 ppm cobalt (as oleate)
16 and 1000 ppm of a photoinitiator (BBP³). The headspace oxygen for the
17 pouches is shown in Table 10. Both of the test oxygen scavenging films
18 scavenged more oxygen than the packaged turkey itself.

19 Table 10

| Oxygen scavenging layer composition | Initial headspace oxygen, % | Headspace oxygen after 3 days @ 4°C, % |
|--|--------------------------------|---|
| none | 1.02 | 0.72 |
| SBS | 1.00 | 0.08 |
| EMCM | 1.02 | 0.17 |

20

21 Taste panelists were instructed to force rank the samples according to their
22 taste preference; assigning the least preferred sample a score of 1, and the

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1 most preferred sample a score of 10. As is shown in Figure 5, the panelists
2 found the taste of the turkey packaged in control and the EMCM pouches
3 statistically equivalent. The turkey packaged in the SBS pouch was found
4 significantly less preferred than either the control or the EMCM.

5 Example 30

6 Polymerization of EMCM via high pressure autoclave reactor proceeds in a
7 steady-state continuous manner as follows. Ethylene is circulated at a rate of
8 10,000-14,000 lb/hr by a hypercompressor which compresses the ethylene to
9 16,500-22,500 psig. The compressed ethylene is injected into the autoclave
10 reactor in various positions along the reactor wall associated with the zone
11 divisions made by the reactor internals. Simultaneously, acrylate of
12 cyclohexene-1-methanol (CHAA) comonomer is injected into either the first
13 zone or the first and second zones of the reactor at a rate sufficient to
14 produce a copolymer containing from 5 to 40% CHAA, more typically
15 10%-25% by weight. The reaction is initiated by injection of a solution of
16 di-tert butyl peroxyvalate in an aliphatic solvent which also functions as a
17 chain transfer agent. The initiator is injected at a rate to provide
18 approximately 10-20 ppm (wt) of initiator in the compressed ethylene.
19 The locations of the CHAA injection are critical to the polymer being
20 produced, as is shown in U.S. Patent No. 5,571,878 which details the effects
21 of acrylate injection location on the polymerization of ethylene and an alkyl
22 acrylate comonomer in a high pressure system.

23
24 The resultant polymer exits the reactor at a rate of 1000-2000 lb/hr in a
25 multi-phase solution in ethylene to a high pressure separator. The pressure
26 of the product is reduced adiabatically through a valve to 2,000 psig pressure
27 and the unreacted ethylene and unreacted CHAA are recompressed to
28 reactor pressure and reinjected into the reactor for further polymerization.
29 Additional ethylene is added to the cycle via a primary compressor which

1 compresses the ethylene from pipeline pressure to the suction pressure of the
2 hypercompressor at a rate equal to the polymer production rate.
3 From the high pressure separator, the polymer is reduced in pressure to
4 4-10 psig for further removal of unreacted ethylene and unreacted
5 comonomer. The polymer is fed into a melt pumping device (either an
6 extruder or a gear pump) and is pelletized and transferred for packaging and
7 shipment.

8

9 Example 3110 Synthesis of 3-Cyclohexene-1,1-Dimethanol

11 One hundred (100) parts by weight of a formaldehyde aqueous solution
12 (37 wt. % formaldehyde) was charged to a reactor. To this solution, cooled
13 externally with an ice-water bath, was added 118 parts of an aqueous sodium
14 hydroxide solution (25 wt. % sodium hydroxide) by several portions and the
15 temperature of the reaction content was maintained at 20 to 30°C. This was
16 followed by a slow addition of 54 parts of 1,2,5,6-tetrahydrobenzaldehyde at
17 such a rate that the reaction content temperature did not exceed 55°C. After
18 the exotherm dissipated, it was heated at 55°C for two hours with an external
19 heating. The product precipitated out of the solution upon cooling and was
20 collected by suction filtration. The wet-cake was washed thoroughly in the
21 funnel with copious amount of water (5 X 100 parts). The crude product was
22 allowed to dry in air overnight and purified by a recrystallization from toluene.
23 The final product was an off-white colored crystalline material (yield 70%.
24 m.p.: 92-93°C).

25

26 Example 3227 Synthesis of 4-Cyclohexene-1,2-Dimethanol

28 A solution of one hundred (100) parts by weight of a 1,2,3,6-
29 tetrahydrophthalic anhydride in 500 parts of dry tetrahydrofuran is slowly
30 added to a stirring mixture of 28.75 parts of lithium aluminum hydride and

1 162 parts of tetrahydrofuran. After the addition is complete, the mixture is
2 refluxed for 24 hours. It is then hydrolyzed by a slow addition of a saturated
3 Rochelle salt solution until it turns white. The mixture is refluxed for an
4 additional 10 hours, allowed to room temperature, and suction filtered. The
5 solvent is removed by a distillation and the viscous liquid crude product is
6 purified by a fractional distillation under vacuum (yield 82%. b.p.: 165-170°C
7 at 12 mm).

8

9 Example 3310 Synthesis of trans-Diethyl 1,2,3,6-Tetrahydrophthalate

11 One hundred (100) parts by weight of a butadiene is dissolved into a solution
12 of 153 parts of diethyl fumarate in 650 parts of benzene at 0°C. The reaction
13 solution is then heated in a bomb at 50°C for 24 hours. The solvent is
14 removed by a distillation and the liquid crude product is purified by a fractional
15 distillation under vacuum (b.p.: 102-105°C at 2 mm).

16

17 Example 3418 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol

19 Dimethyl terephthalate (81.9 g), ethylene glycol (43.7 g), 3-cyclohexene-
20 1,1-dimethanol (20.0 g), and titanium butoxide (0.15 g) were charged into a
21 250 mL 4-necked flask equipped with a distillation column/partial condenser.
22 The agitator and heat were turned on under nitrogen sparge (5 ml/min).
23 When the temperature reached 140-170°C, the methanol collection was
24 started. The temperature was slowly increased to 230°C. The reaction
25 temperature was held at 230-240°C until greater than 95% of the methanol
26 was collected during the course of 2-3 hours at 250-260°C under a full
27 vacuum (0.5-2 mm Hg). The final polyester was discharged into an aluminum
28 pan at about 200°C under nitrogen protection. NMR showed that the
29 polyester contained about 22 wt. % 3-cyclohexene-1,1-dimethanol unit. DSC

1 showed that the polyester was totally amorphous and had a glass transition
2 temperature of 82°C.

3

4 Example 35

5 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol

6 Dimethyl terephthalate (1165.2 g), ethylene glycol (621.0 g), 3-cyclohexene-
7 1,1-dimethanol (284.4 g), zinc acetate dihydrate (2.08 g), and antimony oxide
8 (0.62 g) are charged into a 3-liter reaction kettle equipped with a distillation
9 column/partial condenser. The agitator and heat are turned on under
10 nitrogen sparge (10-30 ml/min). When the temperature reaches 140-170°C,
11 the methanol collection is started. After 1-3 hours at 160-190°C under
12 nitrogen, the temperature is slowly increased to 230°C. The reaction
13 temperature is held at 230-240°C until greater than 95% of the methanol is
14 collected during the course of 2-6 hours. Triphenyl phosphite (1.0 g) is then
15 added. The temperature is increased to 250-270°C, the nitrogen is stopped
16 and vacuum is applied. The reaction mixture is held for 2-4 hours at
17 250-270°C under a full vacuum (0.5-2 mm Hg). The final polyester is
18 discharged into an aluminum pan at about 200°C under nitrogen protection.

19

20 Example 36

21 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol

22 Following the procedure described in Example 35, dimethyl terephthalate
23 (776.8 g), 1,3-propanediol (304.4 g), 3-cyclohexene-1,1-dimethanol (284.4 g),
24 and titanium butoxide (1.3 g) are charged into a 3-liter reaction kettle
25 equipped with a distillation column/partial condenser. Triphenyl phosphite
26 (0.8 g) is added before increasing the reaction temperature from 230-240°C
27 to over 250°C and applying vacuum.

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1 Example 372 Synthesis of Polyester Containing 1,2,3,6-Tetrahydrophthalic Acid

3 Ethylene glycol (248.1 g), 1,2,3,6-tetrahydrophthalic anhydride (456.6 g),
4 hydrated monobutyltin oxide (0.7 g), and triphenyl phosphite (0.35 g) were
5 charged into a 2-liter reaction flask equipped with a distillation column/partial
6 condenser. The agitator and heat are turned on under nitrogen sparge
7 (10-30 ml/min). When the temperature reaches 160-180°C, the water
8 collection was started. After 1-3 hours at 160-190°C under nitrogen, the
9 temperature was slowly increased to 230°C. The reaction temperature was
10 held at 230-240°C until greater than 95% of the water was collected during
11 the course of 2-6 hours. The temperature was increased to 250-270°C, the
12 nitrogen was stopped and vacuum was applied. The reaction mixture was
13 held for 2-4 hours at 250-270°C under a full vacuum (0.5-2 mm Hg). The final
14 polyester was discharged into an aluminum pan at about 200°C under
15 nitrogen protection. NMR confirmed that the polyester was a
16 tetrahydrophthalic acid/ethylene glycol homopolyester. DSC showed that the
17 polyester was totally amorphous and had a glass transition temperature of
18 27°C.

19 Example 38

20 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol
21 and 1,2,3,6-Tetrahydrophthalic Acid

22 Following the procedure described in Example 37, ethylene glycol (248.4 g),
23 1,2,3,6-tetrahydrophthalic anhydride (913.2 g), 3-cyclohexene-1,1-dimethanol
24 (839.0 g), and hydrated monobutyltin oxide (1.0 g) are charged into a 3-liter
25 reaction kettle equipped with a distillation column/partial condenser.
26 Triphenyl phosphite (1.0 g) is added before increasing the reaction
27 temperature from 230-240°C to over 250°C and applying vacuum.

1 Example 39

2 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol
3 and 1,2,3,6-Tetrahydrophthalic Acid

4 Following the procedure described in Example 37, 2-methyl-1,3-propanediol
5 (360.4 g), 1,2,3,6-tetrahydrophthalic anhydride (913.2 g), 3-cyclohexene-
6 1,1-dimethanol (839.0 g), and hydrated monobutyltin oxide (1.0 g) are
7 charged into a 3-liter reaction kettle equipped with a distillation column/partial
8 condenser. Triphenyl phosphite (1.0 g) is added before increasing the
9 reaction temperature from 230-240°C to over 250°C and applying vacuum.

10

11 Example 40

12 Synthesis of Polyester Containing 1,2,3,6-Tetrahydrophthalic Acid

13 Following the procedure described in Example 37, 2 methyl-1,3-propanediol
14 (720.8 g), 1,2,3,6-tetrahydrophthalic anhydride (913.2 g), and hydrated
15 monobutyltin oxide (0.82 g) are charged into a 3-liter reaction kettle equipped
16 with a distillation column/partial condenser. Triphenyl phosphite (0.82 g) is
17 added before increasing the reaction temperature from 230-240°C to over
18 250°C and applying vacuum.

19

20 Example 41

21 Synthesis of Polyester Containing 1,2,3,6-Tetrahydrophthalic Acid

22 Following the procedure described in Example 37, 1,3-propanediol (608.8 g),
23 1,2,3,6-tetrahydrophthalic anhydride (913.2 g), and hydrated monobutyltin
24 oxide (0.76 g) are charged into a 3-liter reaction kettle equipped with a
25 distillation column/partial condenser. Triphenyl phosphite (0.76 g) is added
26 before increasing the reaction temperature from 230-240°C to over 250°C
27 and applying vacuum.

28

29

30

1 Example 42

2 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol

3 Following the procedure described in Example 37, 2-methyl-1,3-propanediol
4 (180.2 g), adipic acid (584.4 g), 3-cyclohexene-1,1-dimethanol (569.6 g), and
5 hydrated monobutyltin oxide (0.67 g) are charged into a 3-liter reaction kettle
6 equipped with a distillation column/partial condenser. Triphenyl phosphite
7 (0.67 g) is added before increasing the reaction temperature from 230-240°C
8 to over 250°C and applying vacuum.

9

10 Example 43

11 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol

12 Terephthalic acid (664.4 g), 3-cyclohexene-1,1-dimethanol (284.8 g),
13 2-methyl-1,3-propandiol (360.4 g), and hydrated monobutyltin oxide (0.75 g)
14 are charged into a 3-liter reaction kettle equipped with a distillation
15 column/partial condenser. The agitator and heat are turned on under
16 nitrogen sparge (10-30 ml/min). When the temperature reaches 200-220°C,
17 the water collection is started. After 3-7 hours at 200-230°C under nitrogen,
18 the temperature is increased to 240°C. The reaction temperature is held at
19 240°C until greater than 95% of the water is collected during the course of
20 2-6 hours. Triphenyl phosphite (0.75 g) is then added. The temperature is
21 increased to 250-270°C, the nitrogen is stopped and vacuum is applied. The
22 reaction mixture is held for 2-4 hours at 250-270°C under a full vacuum
23 (0.5-2 mm Hg). The final polyester is discharged into an aluminum pan at
24 about 200°C under nitrogen protection.

25

26 Example 44

27 Polymer prepared in Example 34 was solvent cast into a 3.5 mil film
28 containing 2 wt. % cobalt in the form of cobalt oleate and 2 wt. % of
29 anthraquinone as a long wavelength photoinitiator. A 5 x 20 cm² size film was

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1 cut and irradiated under a 450 watts medium pressure mercury UV lamp for
2 2 minutes prior to sealing into a foil pouch filled with 300 cc of 1% oxygen.
3 The headspace analysis after 1 day at room temperature showed a reduction
4 in oxygen concentration to 0.91%.

5

6

Example 45

7 Polymer prepared in Example 37 was solvent cast into 2 mil film containing
8 0.2 wt.% cobalt in the form of cobalt oleate and 1 wt.% of anthraquinone.
9 Irradiated under a 450 watts medium pressure mercury UV lamp for 2 minutes
10 prior to sealing into a foil pouch filled with 300 cc of 1% oxygen. The
11 headspace analysis after 4 days at room temperature showed a reduction in
12 oxygen concentration to 0.83%.

13

14 Also included within this example and the scope of the invention are
15 compositions comprising various combinations of these substances and
16 materials.

17

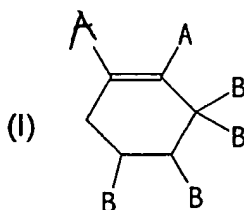
18 Aspects of the present invention have been described by way of example only
19 and it should be appreciated that modifications and additions may be made
20 thereto without departing from the scope thereof.

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1 WHAT IS CLAIMED:

2

- 3 1. A composition suitable for scavenging oxygen comprising a mixture of:
4 (a) a polymer or lower molecular weight material containing
5 substituted cyclohexene functionality according to the following
6 structure (I):



13 where A may be hydrogen or methyl and either one or two of the B groups is
14 a heteroatom containing linkage which attaches the cyclohexene
15 ring to the said material. The remaining B groups are hydrogen or
16 methyl.

16

- 17 (b) a transition metal catalyst.

18

- 19 2. The composition of claim 1 where the material is blended with a carrier
20 resin.

21

- 22 3. The composition according to claim 2 wherein said mixture further
23 contains at least one photoinitiator.

- 24 4. The composition according to claim 1 wherein the heteroatom
25 containing linkage contains an ester, ether, amide, imide, urethane, or acetal
26 group.

27

- 28 5. An oxygen scavenger composition comprising a polymer or oligomer
29 having at least one cyclohexene group, and a transition metal salt, compound
30 or complex.

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- 1 6. The composition of claim 5 further comprising a trigger enhancing
2 component which makes the scavenger susceptible to triggering from an
3 external even.
- 4 7. The composition of claim 6, wherein the trigger enhancing component is
5 selected from the group consisting of benzophenone or substituted
6 benzophenone.
- 7 8. The composition of claim 6, wherein the external event is irradiation by
8 electromagnetic radiation.
- 9 9. The composition of claim 6, wherein the external event is irradiation by
10 UV light.
- 11 10. The composition of claim 5, wherein the material is blended with a
12 carrier resin.
- 13 11. The composition of claim 5, wherein the oxygen scavenger composition
14 is in the form of a plastics resin.
- 15 12. The composition of claim 11, wherein the plastics resin comprises a
16 polyester resin.
- 17 13. The composition of claim 11, wherein the plastics resin comprises a
18 resin suitable for use in the manufacture of plastic films.
- 19 14. The composition of claim 5 wherein the composition is prepared from
20 the reaction of a tetrahydrophthalic anhydride with at least one of:
- 21 i) a diol;
22 ii) a hydroxy compound; or
23 iii) a polyhydroxy compound.
- 24 15. The composition of claim 14 wherein the composition is prepared by
25 heating tetrahydrophthalic anhydride with at least one of:
- 26 i) a diol;
27 ii) a hydroxy compound; or
28 iii) a polyhydroxy compound,
29 in a solvent.
30

- 1 16. The oxygen scavenger composition of claim 14 wherein the anhydride
2 comprises 1,2,3,6 tetrahydrophthalic anhydride, or tetrahydrophthalic
3 anhydride monomer derivable from butadiene.
- 4 17. The composition of claim 14 wherein the composition is prepared by a
5 reactive extrusion process.
- 6 18. The composition of claim 5 prepared from the reaction of a
7 tetrahydrobenzyl alcohol with one or more compounds having one or more of
8 the following functionalities:
- 9 i) carboxylic acid;
 - 10 ii) acid halide;
 - 11 iii) ester;
 - 12 iv) anhydride; and
 - 13 v) isocyanate.
- 14 19. The oxygen scavenger composition of claim 18 wherein the composition
15 is prepared by a reactive extrusion process.
- 16 20. The oxygen scavenger composition of claim 18 wherein the composition
17 is prepared from the reaction of a tetrahydrobenzyl alcohol with an ester by a
18 transesterification process.
- 19 21. The oxygen scavenger composition of claim 18 wherein the compound
20 with the anhydride functionality comprises styrene maleic anhydride
21 copolymer.
- 22 22. The oxygen scavenger composition of claim 18 wherein the compound
23 with the isocyanate functionality comprises polyfunctional isocyanate.
- 24 23. The oxygen scavenger composition of claim 5 comprising a polyester,
25 wherein the composition is prepared from cyclohexene dimethanol.
- 26 24. The oxygen scavenger composition of claim 5, wherein the composition
27 is prepared from tetrahydrobenzoic acid and a hydroxyl functional material.
- 28 25. The oxygen scavenger composition of claim 5, wherein the composition
29 is prepared from tetrahydrobenzoic acid and a hydroxyl functional material.

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- 1 26. The oxygen scavenger composition of claim 5, wherein the composition
2 is prepared from tetrahydrobenzaldehyde and a hydroxyl functional material.
- 3 27. The oxygen scavenger composition of claim 5 comprising a polymer or
4 oligomer having at least one cyclohexene group, wherein some carbons of
5 the cyclohexene group form part of other ring structures within the polymer or
6 oligomer.
- 7 28. The oxygen scavenger composition of claim 5 comprising a pendant
8 cyclic alkene group, the composition prepared by a method wherein some
9 carbons of the cyclohexene group form part of the skeleton of the polymer or
10 oligomer.
- 11 29. The oxygen scavenger composition of claim 5, comprising a pendant
12 cyclohexene group, wherein the composition is prepared by a method
13 including a Diels Alder addition reaction.
- 14 30. The oxygen scavenger composition of claim 5 wherein the composition
15 is incorporated in a sachet.

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1
2 31. A composition comprising a polymeric backbone, cyclic olefinic pendent
3 groups and linking groups linking the olefinic pendent groups to the polymeric
4 backbone.

5 32. A composition according to claim 31, wherein the polymeric backbone is
6 ethylenic and the linking groups are selected from the group consisting
7 of:

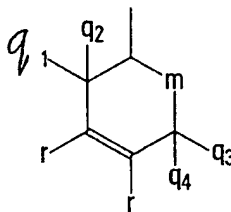
8 $-\text{O}-(\text{CHR})_n-$; $-(\text{C}=\text{O})-\text{O}-(\text{CHR})_n-$; $-\text{NH}-(\text{CHR})_n-$; $-\text{O}-(\text{C}=\text{O})-(\text{CHR})_n-$;

9 $-(\text{C}=\text{O})-\text{NH}-(\text{CHR})_n-$; and $-(\text{C}=\text{O})-\text{O}-\text{CHOH}-\text{CH}_2-\text{O}-$;

10 wherein R is hydrogen or an alkyl group selected from the group
11 consisting of methyl, ethyl, propyl and butyl groups and where n is an
12 integer in the range from 1 to 12.

13 33. The composition of claim 31, wherein the cyclic olefinic pendent groups
14 have the structure (II):

15 (II)

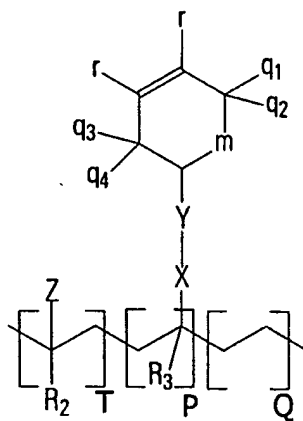


16
17
18 where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-\text{H}$, $-\text{CH}_3$, and $-\text{C}_2\text{H}_5$; and where m is $-(\text{CH}_2)_n-$ with n being an integer in the
19 range from 0 to 4; and wherein, when r is $-\text{H}$, at least one of q_1 , q_2 , q_3
20 and q_4 is $-\text{H}$.
21

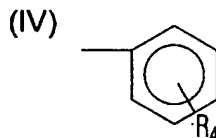
- 1 38. The composition of claim 31, wherein the polymeric backbone
2 comprises monomers selected from the group consisting of ethylene
3 and styrene.
4
- 5 38. The composition of claim 31, wherein the cyclic olefinic pendent groups
6 are grafted onto the linking groups of the polymeric backbone by an
7 esterification, transesterification, amidation or transamidation reaction.
- 8 38. The composition of claim 35, wherein the esterification,
9 transesterification, amidation or transamidation reaction is a solution
10 reaction or a reactive extrusion.
- 11 38. The composition of claim 35, wherein the esterification,
12 transesterification, amidation or transamidation reaction is catalyzed by
13 a catalyst selected from the group consisting of strong non-oxidizing
14 acids, tertiary amines, Group I alkoxides, Group IVB alkoxides, and
15 Group IVA organometallics.
- 16 38. The composition of claim 37, wherein the catalyst is selected from a
17 group consisting of toluene sulfonic acid, sodium methoxide, tetrabutyl
18 titanate, tetraisopropyl titanate, tetra-n-propyl-titanate, tetraethyl titanate,
19 2-hydroxy-pyridine and dibutyltin dilaurate.
- 20 39. The composition of claim 31, wherein the polymeric backbone, linking
21 groups and cyclic olefin pendent groups comprise repeating units, each unit
22 having a structure (III) as follows:

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(III)



wherein $P+T+Q$ is 100 mol % of the total composition; P is greater than 0 mol % of the total composition; Z is selected from the group consisting of an aryl group; $-(C=O)OR_1$; $-O(C=O)R_1$; and an alkyl aryl group, structure(IV):



where R_4 is selected from the group consisting of $-CH_3$, $-C_2H_5$, and $-H$; R_1 is selected from the group consisting of $-H$, $-CH_3$, $-C_2H_5$, $-C_3H_7$ and $-C_4H_9$; R_2 and R_3 are selected from the group consisting of $-H$ and $-CH_3$; X is selected from the group consisting of $-O-$, $-NH-$, $-(C=O)O-$, $-(C=O)NH-$, $-(C=O)S-$, $-O(C=O)-$ and $-(CHR)_\ell$; ℓ is an integer in the range from 1 to 6; Y is $-(CHR)_n$, where n is an integer in the range from 0 to 12, R being selected from the group consisting of $-H$, $-CH_3$ and $-C_2H_5$; where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$,

1 and $-C_2H_5$; and where m is $-(CH_2)_n-$ and where n is an integer in the
2 range from 0 to 4; and wherein when r is $-H$, at least one of q_1 , q_2 , q_3
3 and q_4 is $-H$.

4 40. The composition of claim 39, wherein the cyclic olefinic pendent groups
5 are selected from the group consisting of cyclohexene-4-methylene radical,
6 1-methyl cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-
7 methylene radical, 5-methyl cyclohexene-4-methylene radical, 1,2-dimethyl
8 cyclohexene-4-methylene radical, 1,5-dimethyl cyclohexene-4-methylene
9 radical, 2,5-dimethyl cyclohexene-4-methylene radical, 1,2,5-trimethyl
10 cyclohexene-4-methylene radical, cyclohexene-4-ethylene radical, 1-methyl
11 cyclohexene-4-ethylene radical, 2-methyl cyclohexene-4-ethylene radical,
12 5-methyl cyclohexene-4-ethylene radical, 1,2-dimethyl cyclohexene-4-
13 ethylene radical, 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl
14 cyclohexene-4-ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene
15 radical, cyclohexene-4-propylene radical, 1-methyl cyclohexene-4-propylene
16 radical, 2-methyl cyclohexene-4-propylene radical, 5-methyl cyclohexene-4-
17 propylene radical, 1,2-dimethyl cyclohexene-4-propylene radical, 1,5-dimethyl
18 cyclohexene-4-propylene radical, 2,5-dimethyl cyclohexene-4-propylene
19 radical, 1,2,5-trimethyl cyclohexene-4-propylene radical, cyclopentene-4-
20 methylene radical, 1-methyl cyclopentene-4-methylene radical, 3-methyl
21 cyclopentene-4-methylene radical, 1,2-dimethyl cyclopentene-4-methylene
22 radical, 3,5-dimethyl cyclopentene-4-methylene radical, 1,3-dimethyl
23 cyclopentene-4-methylene radical, 2,3-dimethyl cyclopentene-4-methylene
24 radical, 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
25 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-methyl
26 cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-ethylene radical,
27 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-dimethyl cyclopentene-4-
28 ethylene radical, 1,3-dimethyl cyclopentene-4-ethylene radical, 2,3-dimethyl
29 cyclopentene-4-ethylene radical, 1,2,3-trimethyl cyclopentene-4-ethylene

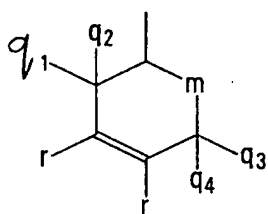
-123-

1 radical, 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-
 2 propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl
 3 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-propylene
 4 radical, 3,5-dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl
 5 cyclopentene-4-propylene radical, 2,3-dimethyl cyclopentene-4-propylene
 6 radical, 1,2,3-trimethyl cyclopentene-4-propylene radical, and 1,2,3,5-
 7 tetramethyl cyclopentene-4-propylene radical.

- 8 41. The composition of claim 39, wherein the composition is an
 9 ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer, a
 10 cyclohexenyl methyl acrylate/ethylene copolymer, a cyclohexenyl methyl
 11 methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate
 12 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate copolymer.
- 13 42. An oxygen scavenging composition comprising a polymeric backbone,
 14 cyclic olefinic pendent groups, linking groups linking the olefinic pendent
 15 groups to the polymeric backbone and a transition metal catalyst.
- 16 43. A composition according to claim 42, wherein the polymeric backbone is
 17 ethylenic and the linking groups are selected from the group consisting
 18 of:
- 19 $-\text{O}-(\text{CHR})_n-$; $-(\text{C}=\text{O})-\text{O}-(\text{CHR})_n-$; $-\text{NH}-(\text{CHR})_n-$; $-\text{O}-(\text{C}=\text{O})-(\text{CHR})_n-$;
 20 $-(\text{C}=\text{O})-\text{NH}-(\text{CHR})_n-$; and $-(\text{C}=\text{O})-\text{O}-\text{CHOH}-\text{CH}_2-\text{O}-$;
- 21 wherein R is hydrogen or an alkyl group selected from the group
 22 consisting of methyl, ethyl, propyl and butyl groups and where n is an
 23 integer in the range from 1 to 12.
- 24 44. The composition of claim 42, wherein the cyclic olefinic pendent groups
 25 have the structure (II):

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(II)



7 where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$,
 8 and $-C_2H_5$; and where m is $-(CH_2)_n-$ with n being an integer in the range
 9 from 0 to 4; and wherein, when r is $-H$, at least one of q_1 , q_2 , q_3 and q_4 is
 10 $-H$.

11 45. The composition of claim 42, wherein the polymeric backbone
 12 comprises monomers selected from the group consisting of ethylene
 13 and styrene.

14 46. The composition of claim 42, wherein the cyclic olefinic pendent groups
 15 are grafted onto the linking groups of the polymeric backbone by a
 16 esterification, transesterification, amidation or transamidation reaction.

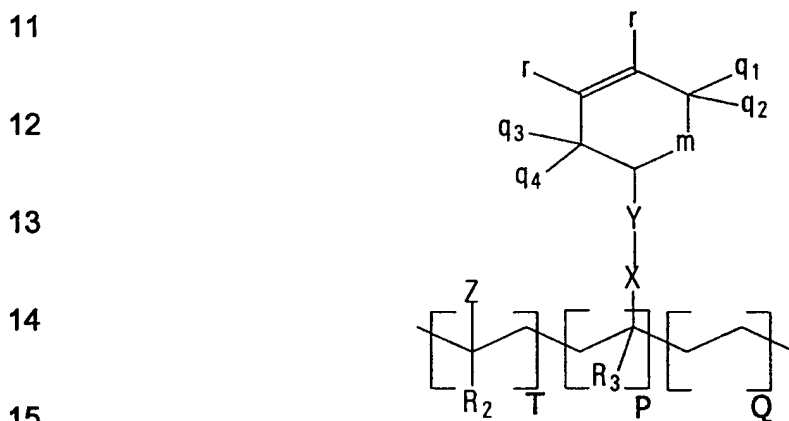
17 47. The composition of claim 46, wherein the esterification,
 18 transesterification, amidation or transamidation reaction is a solution
 19 reaction or a reactive extrusion.

20 48. The composition of claim 46, wherein the esterification,
 21 transesterification, amidation or transamidation reaction is catalyzed by
 22 a catalyst selected from the group consisting of strong non-oxidizing

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- 1 acids, tertiary amines, Group I alkoxides, Group IVB alkoxides, and
 2 Group IVA organometallics.
- 3 49. The composition of claim 48, wherein the catalyst is selected from a
 4 group consisting of toluene sulfonic acid, sodium methoxide, tetrabutyl
 5 titanate, tetraisopropyl titanate, tetra-n-propyl-titanate, tetraethyl titanate,
 6 2-hydroxy-pyridine and dibutyltin dilaurate.
- 7 50. The composition of claim 42, wherein the polymeric backbone, linking
 8 groups and cyclic olefin pendent groups comprise repeating units, each
 9 unit having a structure (III) as follows:

10 (III)



- 16 wherein $P + T + Q$ is 100 mol % of the total composition; P is greater than 0
 17 mol % of the total composition; Z is selected from the group consisting
 18 of an aryl group; $-(C=O)OR_1$; $-O(C=O)R_1$; and an alkyl aryl group,
 19 structure (IV):



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1 where R_4 is selected from the group consisting of $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, and $-\text{H}$; R_1 is
 2 selected from the group consisting of $-\text{H}$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$ and $-\text{C}_4\text{H}_9$;
 3 R_2 and R_3 are selected from the group consisting of $-\text{H}$ and $-\text{CH}_3$; X is
 4 selected from the group consisting of $-\text{O}-$, $-\text{NH}-$, $-(\text{C}=\text{O})\text{O}-$, $-(\text{C}=\text{O})\text{NH}-$,
 5 $-(\text{C}=\text{O})\text{S}-$, $-\text{O}(\text{C}=\text{O})-$ and $-(\text{CHR})_\ell-$; ℓ is an integer in the range from 1 to
 6 6; Y is $-(\text{CHR})_n-$, where n is an integer in the range from 0 to 12, R being
 7 selected from the group consisting of $-\text{H}$, $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$; where q_1 , q_2 ,
 8 q_3 , q_4 , and r are selected from the group consisting of $-\text{H}$, $-\text{CH}_3$, and
 9 $-\text{C}_2\text{H}_5$; and where m is $-(\text{CH}_2)_n-$ and where n is an integer in the range
 10 from 0 to 4; and wherein when r is $-\text{H}$, at least one of q_1 , q_2 , q_3 and q_4 is
 11 $-\text{H}$.

12 51. The composition of claim 50, wherein the cyclic olefinic pendent groups
 13 are selected from the group consisting of cyclohexene-4-methylene
 14 radical, 1-methyl cyclohexene-4-methylene radical, 2-methyl
 15 cyclohexene-4-methylene radical, 5-methyl cyclohexene-4-methylene
 16 radical, 1,2-dimethyl cyclohexene-4-methylene radical, 1,5-dimethyl
 17 cyclohexene-4-methylene radical, 2,5-dimethyl cyclohexene-4-
 18 methylene radical, 1,2,5-trimethyl cyclohexene-4-methylene radical,
 19 cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-ethylene
 20 radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl cyclohexene-
 21 4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene radical, 1,5-
 22 dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-4-
 23 ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene radical,
 24 cyclohexene-4-propylene radical, 1-methyl cyclohexene-4-propylene
 25 radical, 2-methyl cyclohexene-4-propylene radical, 5-methyl
 26 cyclohexene-4-propylene radical, 1,2-dimethyl cyclohexene-4-propylene
 27 radical, 1,5-dimethyl cyclohexene-4-propylene radical, 2,5-dimethyl
 28 cyclohexene-4-propylene radical, 1,2,5-trimethyl cyclohexene-4-
 29 propylene radical, cyclopentene-4-methylene radical, 1-methyl

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1 cyclopentene-4-methylene radical, 3-methyl cyclopentene-4-methylene
2 radical, 1,2-dimethyl cyclopentene-4-methylene radical, 3,5-dimethyl
3 cyclopentene-4-methylene radical, 1,3-dimethyl cyclopentene-4-
4 methylene radical, 2,3-dimethyl cyclopentene-4-methylene radical, 1,2,3-
5 trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
6 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-
7 methyl cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-
8 ethylene radical, 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-
9 dimethyl cyclopentene-4-ethylene radical, 1,3-dimethyl cyclopentene-4-
10 ethylene radical, 2,3-dimethyl cyclopentene-4-ethylene radical, 1,2,3-
11 trimethyl cyclopentene-4-ethylene radical, 1,2,3,5-tetramethyl
12 cyclopentene-4-ethylene radical, cyclopentene-4-propylene radical, 1-
13 methyl cyclopentene-4-propylene radical, 3-methyl cyclopentene-4-
14 propylene radical, 1,2-dimethyl cyclopentene-4-propylene radical, 3,5-
15 dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl cyclopentene-4-
16 propylene radical, 2,3-dimethyl cyclopentene-4-propylene radical, 1,2,3-
17 trimethyl cyclopentene-4-propylene radical, and 1,2,3,5-tetramethyl
18 cyclopentene-4-propylene radical.

19 52. The composition of claim 50, wherein the composition is an
20 ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer, a
21 cyclohexenyl methyl acrylate/ethylene copolymer, a cyclohexenyl methyl
22 methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate
23 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate copolymer.

24 53. The composition of claim 42, wherein odor and taste characteristics of
25 products packaged with material comprised of the composition are not
26 adulterated as a result of oxidation of the composition.

27 54. The composition of claim 42, wherein there is no significant
28 fragmentation of the olefinic pendent groups and linking groups from the
29 polymeric backbone as a result of oxidation of the composition.

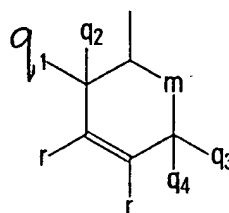
- 1 54. The composition of claim 42, wherein there is no significant
2 fragmentation of the olefinic pendent groups and linking groups from the
3 polymeric backbone as a result of oxidation of the composition.
- 4 55. The composition of claim 42, wherein the transition metal catalyst is a
5 metal salt.
- 6 56. The composition of claim 55, wherein the metal in the metal salt is
7 cobalt.
- 8 57. The composition according to claim 55, wherein the metal salt is
9 selected from the group consisting of cobalt neodecanoate, cobalt
10 2-ethylhexanoate, cobalt oleate and cobalt stearate.
- 11 58. The composition of claim 42, further comprising at least one triggering
12 material to enhance initiation of oxygen scavenging.
- 13 59. The composition of claim 58, wherein the triggering material is a photo
14 initiator.
- 15 60. An article of manufacture suitable as a container, the container inhibiting
16 oxidation of contents of the container by removing oxygen from the
17 container and by inhibiting ingress of oxygen into the container from
18 outside the container, wherein the article comprises an oxygen
19 scavenging composition which comprises a polymeric backbone, cyclic
20 olefinic pendent groups, linking groups linking the olefinic pendent
21 groups to the backbone, and a transition metal catalyst.
- 22 61. The article of manufacture of claim 60, wherein the polymeric backbone
23 is ethylenic and the linking groups are selected from the group
24 consisting of:
- 25 $\text{-O-(CHR)}_n\text{-}$; $\text{-(C=O)-O-(CHR)}_n\text{-}$; $\text{-NH-(CHR)}_n\text{-}$; $\text{-O-(C=O)-(CHR)}_n\text{-}$;
- 26 $\text{-(C=O)-NH-(CHR)}_n\text{-}$; and $\text{-(C=O)-O-CHOH-CH}_2\text{-O-}$;

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1 wherein R is hydrogen or an alkyl group selected from the group
2 consisting of methyl, ethyl, propyl and butyl groups and where n is an
3 integer in the range from 1 to 12.

4 62. The article of manufacture of claim 60, wherein the cyclic olefinic
5 pendent groups have the structure (II):

6 (II)



7
8
9
10 where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$,
11 and $-C_2H_5$; and where m is $-(CH_2)_n-$ and where n is an integer in the
12 range of from 0 to 4; and wherein when r is $-H$, at least one of q_1 , q_2 , q_3
13 and q_4 is also $-H$.

14 63. The article of manufacture of claim 60, wherein the polymeric backbone
15 comprises monomers selected from the group consisting of ethylene and
16 styrene.

17 64. The article of manufacture of claim 60, wherein the cyclic olefinic
18 pendent groups are grafted onto the linking groups of the polymeric
19 backbone by a esterification, transesterification, amidation or
20 transamidation reaction.

21 65. The article of manufacture of claim 64, wherein the esterification,
22 transesterification, amidation or transamidation reaction is a solution
23 reaction or a reactive extrusion.

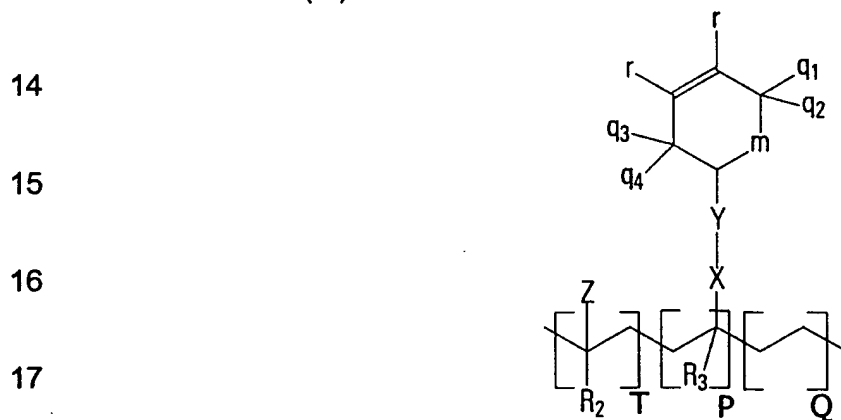
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1 66. The article of manufacture of claim 64, wherein the esterification,
 2 transesterification, amidation or transamidation reaction is catalyzed by
 3 a catalyst selected from the group consisting of strong non-oxidizing
 4 acids, tertiary amines, Group I alkoxides, Group IVB alkoxides, and
 5 Group IVA organometallics.

6 67. The article of manufacture of claim 66, wherein the catalyst is selected
 7 from the group consisting of toluene sulfonic acid, sodium methoxide,
 8 tetrabutyl titanate, tetraisopropyl titanate, tetra-n-propyl-titanate,
 9 tetraethyl titanate, 2-hydroxy-pyridine and dibutyltin dilaurate.

10 68. The article of manufacture of claim 60, wherein the backbone, linking
 11 groups and cyclic olefin pendent groups comprise repeating units, each
 12 unit having a structure (III) as follows:

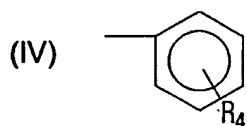
13 (III)



19 wherein $P+T+Q$ is 100 mol % of the total composition; P is greater than 0
 20 mol % of the total composition; Z is selected from the group consisting
 21 of an aryl group, $-(C=O)OR_1$, $-O(C=O)R_1$ and an alkyl aryl group,
 22 structure (IV):

23

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where R_4 is selected from the group consisting of $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, and $-\text{H}$; R_1 is selected from the group consisting of $-\text{H}$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$ and $-\text{C}_4\text{H}_9$; R_2 and R_3 are selected from the group consisting of $-\text{H}$ and CH_3 ; X is selected from the group consisting of $\text{O}-$, $-\text{NH}-$, $-(\text{C}=\text{O})\text{O}-$, $-(\text{C}=\text{O})\text{NH}-$, $-(\text{C}=\text{O})\text{S}-$, $-\text{O}(\text{C}=\text{O})-$ and $-(\text{CHR})_\ell-$; ℓ is an integer selected from the group consisting of 1, 2, 3, 4, 5 and 6; Y is $-(\text{CHR})_n-$, where n is an integer in the range from 0 to 12 and R is selected from the group consisting of $-\text{H}$, $-\text{CH}_3$ and C_2H_5 ; and where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-\text{H}$, $-\text{CH}_3$, and $-\text{C}_2\text{H}_5$; and where m is $-(\text{CH}_2)_n-$ and where n is an integer in the range of from 0 to 4; and wherein when r is $-\text{H}$, at least one of q_1 , q_2 , q_3 , and q_4 is $-\text{H}$.

69. The article of manufacture of claim 60, wherein the cyclic olefinic pendent groups are selected from the group consisting of cyclohexene-4-methylene radical, 1-methyl cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-methylene radical, 5-methyl cyclohexene-4-methylene radical, 1,2-dimethyl cyclohexene-4-methylene radical, 1,5-dimethyl cyclohexene-4-methylene radical, 2,5-dimethyl cyclohexene-4-methylene radical, 1,2,5-trimethyl cyclohexene-4-methylene radical, cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-ethylene radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl cyclohexene-4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene radical, 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-4-ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene

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1 radical, cyclohexene-4-propylene radical, 1-methyl cyclohexene-4-propylene
2 radical, 2-methyl cyclohexene-4-propylene radical, 5-methyl cyclohexene-4-
3 propylene radical, 1,2-dimethyl cyclohexene-4-propylene radical, 1,5-dimethyl
4 cyclohexene-4-propylene radical, 2,5-dimethyl cyclohexene-4-propylene
5 radical, 1,2,5-trimethyl cyclohexene-4-propylene radical, cyclopentene-4-
6 methylene radical, 1-methyl cyclopentene-4-methylene radical, 3-methyl
7 cyclopentene-4-methylene radical, 1,2-dimethyl cyclopentene-4-methylene
8 radical, 3,5-dimethyl cyclopentene-4-methylene radical, 1,3-dimethyl
9 cyclopentene-4-methylene radical, 2,3-dimethyl cyclopentene-4-methylene
10 radical, 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
11 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-methyl
12 cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-ethylene radical,
13 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-dimethyl cyclopentene-4-
14 ethylene radical, 1,3-dimethyl cyclopentene-4-ethylene radical, 2,3-dimethyl
15 cyclopentene-4-ethylene radical, 1,2,3-trimethyl cyclopentene-4-ethylene
16 radical, 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-
17 propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl
18 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-propylene
19 radical, 3,5-dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl
20 cyclopentene-4-propylene radical, 2,3-dimethyl cyclopentene-4-propylene
21 radical, 1,2,3-trimethyl cyclopentene-4-propylene radical, and 1,2,3,5-
22 tetramethyl cyclopentene-4-propylene radical.

23 70. The article of manufacture of claim 60, wherein the composition is an
24 ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer, a
25 cyclohexenyl methyl acrylate/ethylene copolymer, a cyclohexenyl methyl
26 methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate
27 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate copolymer.
28

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1 71. The article of manufacture according to claim 60, wherein the transition
2 metal catalyst is a metal salt.

3

4

5 72. The article of manufacture according to claim 71, wherein the metal in
6 the metal salt is cobalt.

7

8 73. The article of manufacture of according to claim 71, wherein the metal
9 salt is selected from the group consisting of cobalt neodecanoate, cobalt
10 2-ethylhexanoate, cobalt oleate and cobalt stearate.

11

12

13 74. The article of manufacture of claim 60, further comprising at least one
14 triggering material to enhance initiation of oxygen scavenging.

15

16 75. The article of manufacture of claim 74, wherein the triggering material is
17 a photoinitiator.

18

19

20 76. The article of manufacture of claim 60, wherein odor and taste
21 characteristics of products packaged with material comprised of the
22 composition are not adulterated as a result of oxidation of the composition.

23

24 77. The article of manufacture of claim 60, wherein there is no significant
25 fragmentation of the olefinic pendent groups and linking groups from the
26 polymeric backbone as a result of oxidation of the composition.

27

28 78. The article of manufacture of claim 60 wherein the article is a
29 package.

30

1 79. The article of manufacture of claim 78, wherein the package
2 comprises a flexible film having a thickness of at most 10 mil or a flexible
3 sheet having a thickness of at least 10 mil.

4
5 80. The article of manufacture of claim 78, wherein the oxygen
6 scavenging system of the package comprises at least one additional layer
7 selected from among oxygen barrier layers, polymeric selective layers, and
8 heat seal layers.

9
10 81. The article of manufacture of claim 78, wherein the article is a
11 package with a food product located within the package.

12 82. The article of manufacture of claim 78, wherein the article is a
13 package for packaging a cosmetic, chemical, electronic device, pesticide or a
14 pharmaceutical composition.

15
16 83. A multi-layer film comprising the article of manufacture according to
17 claim 60, and at least one additional functional layer.

18
19 84. The multi-layer film according to claim 83, wherein at least one
20 additional layer is selected from among oxygen barrier layers, polymeric
21 selective barrier layers, structural layers and heat seal layers.

22
23 85. The multi-layer film according to claim 83, wherein the at least one
24 additional layer is an oxygen barrier layer.

25
26 86. The multi-layer film according to claim 85, further comprising at least
27 one polymeric selective barrier layer.

28
29 87. The multi-layer film according to claim 85, further comprising at least
30 one heat seal layer.

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1

2 88. The multi-layer film according to claim 85, further comprising at least
3 one structural layer.

4

5 89. The article of claim 60, wherein the article is a rigid container, sealing
6 gasket, patch, container closure device, bottle cap, bottle cap insert or
7 molded or thermoformed shape.

8

9 90. The article of claim 89, wherein the molded or thermoformed shape is
10 a bottle or tray.

11

12 91. A layer suitable for scavenging oxygen comprising:

13 i) a polymer backbone;

14 ii) cyclic olefinic pendent groups;

15 iii) linking groups linking the backbone with the pendent groups; and

16 iv) a transition metal catalyst.

17

18 92. The layer of claim 91, wherein odor and taste characteristics of
19 products packaged with material comprised of the layer are not adulterated as
20 a result of oxidation of the layer.

21

22 93. The layer of claim 91, wherein there is no significant fragmentation of
23 the olefinic pendent groups and linking groups from the polymeric backbone
24 as a result of oxidation of the layer.

25

26 94. A layer according to claim 91, wherein the transition metal catalyst is
27 a metal salt.

28

29 95. A layer according to claim 94, wherein the transition metal in the
30 metal salt is cobalt.

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1

2 96. A layer according to claim 94, wherein the metal salt selected from
3 the group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate, cobalt
4 oleate and cobalt stearate.

5

6 97. A layer according to claim 91, wherein said layer in addition
7 comprises polymeric diluent.

8

9 98. A layer according to claim 97, wherein said diluent is a thermoplastic
10 polymer.

11 99. A layer according to claim 91, wherein said layer is adjacent to one or
12 more additional layers.

13

14 100. A layer according to claim 99, wherein at least one additional layer is
15 an oxygen barrier.

16

17 101. A layer according to claim 100, wherein said oxygen barrier
18 comprises a member of the group consisting of poly(ethylene-vinyl alcohol),
19 polyacrylonitrile, poly(vinyl chloride), polyamides, poly(vinylidene dichloride),
20 poly(ethylene terephthalate), silica, metal foil and metalized polymeric films.

21

22 102. A layer according to claim 99, wherein one or more of said additional
23 layer or layers is coextruded with said layer.

24

25 103. A layer according to claim 99, wherein one or more of said additional
26 layer or layers is laminated onto said layer.

27

28 104. A layer according to claim 99, wherein one or more of said additional
29 layer or layers is coated onto said layer.

30

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1 105. A layer according to claim 99, wherein said layer is flexible.

2

3 106. A layer according to claim 99, wherein said layer is transparent.

4

5 107. An article for packaging wherein the article comprises a layer
6 according to claim 91.

7

8 108. A process of making a polymer material by a process selected from
9 the group consisting of esterification, transesterification, amidation,
10 transamidation and direct polymerization, wherein the polymer material
11 comprises a polymer backbone, cyclic olefinic pendent groups, linking groups
12 linking the backbone with the pendent groups.

13 109. The process of claim 108, wherein making the polymer material
14 comprises the steps of:

15 a) selecting polymers from the group consisting of styrene/maleic
16 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
17 ethylene/methacrylic acid, acrylic acid, methacrylic acid, styrene/methacrylic
18 acid, ethylene/methyl acrylate, ethylene/ethyl acrylate, ethylene/butyl acrylate,
19 methyl methacrylate, methyl acrylate, and styrene/methyl methacrylate to
20 form a mixture and combining the polymers with a esterifying/transesterifying
21 compound selected from the group consisting of cyclohexene-4-methanol,
22 1-methyl cyclohexene-4-methanol, 2-methyl cyclohexene-4-methanol,
23 5-methyl cyclohexene-4-methanol, 1,2-dimethyl cyclohexene-4-methanol,
24 1,5-dimethyl cyclohexene-4-methanol, 2,5-dimethyl cyclohexene-4-methanol,
25 1,2,5-trimethyl cyclohexene-4-methanol, cyclohexene-4-ethanol, 1-methyl
26 cyclohexene-4-ethanol, 2-methyl cyclohexene-4-ethanol, 5-methyl
27 cyclohexene-4-ethanol, 1,2-dimethyl cyclohexene-4-ethanol, 1,5-dimethyl
28 cyclohexene-4-ethanol, 2,5-dimethyl cyclohexene-4-ethanol, 1,2,5-trimethyl

1 cyclohexene-4-ethanol, cyclohexene-4-propanol, 1-methyl cyclohexene-4-
2 propanol, 2-methyl cyclohexene-4-propanol, 5-methyl cyclohexene-4-
3 propanol, 1,2-dimethyl cyclohexene-4-propanol, 1,5-dimethyl cyclohexene-4-
4 propanol, 2,5-dimethyl cyclohexene-4-propanol, 1,2,5-trimethyl cyclohexene-
5 4-propanol, cyclopentene-4-methanol, 1-methyl cyclopentene-4-methanol, 3-
6 methyl cyclopentene-4-methanol, 1,2-dimethyl cyclopentene-4-methanol, 3,5-
7 dimethyl cyclopentene-4-methanol, 1,3-dimethyl cyclopentene-4-methanol,
8 2,3-dimethyl cyclopentene-4-methanol, 1,2,3-trimethyl cyclopentene-4-
9 methanol, 1,2,3,5-tetramethyl cyclopentene-4-methanol, cyclopentene-4-
10 ethanol, 1-methyl cyclopentene-4-ethanol, 3-methyl cyclopentene-4-ethanol,
11 1,2-dimethyl cyclopentene-4-ethanol, 3,5-dimethyl cyclopentene-4-ethanol,
12 1,3-dimethyl cyclopentene-4-ethanol, 2,3-dimethyl cyclopentene-4-ethanol,
13 1,2,3-trimethyl cyclopentene-4-ethanol, 1,2,3,5-tetramethyl cyclopentene-4-
14 ethanol, cyclopentene-4-propanol, 1-methyl cyclopentene-4-propanol, 3-
15 methyl cyclopentene-4-propanol, 1,2-dimethyl cyclopentene-4-propanol, 3,5-
16 dimethyl cyclopentene-4-propanol, 1,3-dimethyl cyclopentene-4-propanol,
17 2,3-dimethyl cyclopentene-4-propanol, 1,2,3-trimethyl cyclopentene-4-
18 propanol, and 1,2,3,5-tetramethyl cyclopentene-4-propanol;

19 b) heating the polymers and esterifying/transesterifying compounds
20 selected in (a) to form a polymer melt;

21 c) processing the melt in an extruder under esterification/transesterification
22 conditions with esterification/transesterification catalysts and antioxidants
23 protecting the melt from oxidation during extrusion, so that the polymer melt
24 undergoes esterification of polymeric anhydrides with cyclic olefin pendent
25 groups, esterification of polymeric acids with cyclic olefin pendent groups or
26 exchange of alkyl groups of polymeric esters with cyclic olefin pendent
27 groups; and

28 d) removing volatile organic products and by-products from the melt.

1 110. The process of claim 108, wherein making the polymer material
2 comprises the steps of:

3 a) selecting polymers from the group consisting of styrene/maleic
4 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
5 ethylene/methacrylic acid, acrylic acid, methacrylic acid, styrene/methacrylic
6 acid, ethylene/methyl acrylate, ethylene/ethyl acrylate, ethylene/butyl acrylate,
7 methyl methacrylate, methyl acrylate, and styrene/methyl methacrylate to
8 form a mixture and combining the polymers with a amidizing/transamidizing
9 compound selected from the group consisting of cyclohexene-4-methyl
10 amine, 1-methyl cyclohexene-4-methyl amine, 2-methyl cyclohexene-4-methyl
11 amine, 5-methyl cyclohexene-4-methyl amine, 1,2-dimethyl cyclohexene-4-
12 methyl amine, 1,5-dimethyl cyclohexene-4-methyl amine, 2,5-dimethyl
13 cyclohexene-4-methyl amine, 1,2,5-trimethyl cyclohexene-4-methyl amine,
14 cyclohexene-4-ethyl amine, 1-methyl cyclohexene-4-ethyl amine, 2-methyl
15 cyclohexene-4-ethyl amine, 5-methyl cyclohexene-4-ethyl amine, 1,2-dimethyl
16 cyclohexene-4-ethyl amine, 1,5-dimethyl cyclohexene-4-ethyl amine, 2,5-
17 dimethyl cyclohexene-4-ethyl amine, 1,2,5-trimethyl cyclohexene-4-ethyl
18 amine, cyclohexene-4-propyl amine, 1-methyl cyclohexene-4-propyl amine, 2-
19 methyl cyclohexene-4-propyl amine, 5-methyl cyclohexene-4-propyl amine,
20 1,2-dimethyl cyclohexene-4-propyl amine, 1,5-dimethyl cyclohexene-4-propyl
21 amine, 2,5-dimethyl cyclohexene-4-propyl amine, 1,2,5-trimethyl
22 cyclohexene-4-propyl amine, cyclopentene-4-methyl amine, 1-methyl
23 cyclopentene-4-methyl amine, 3-methyl cyclopentene-4-methyl amine, 1,2-
24 dimethyl cyclopentene-4-methyl amine, 3,5-dimethyl cyclopentene-4-methyl
25 amine, 1,3-dimethyl cyclopentene-4-methyl amine, 2,3-dimethyl
26 cyclopentene-4-methyl amine, 1,2,3-trimethyl cyclopentene-4-methyl amine,
27 1,2,3,5-tetramethyl cyclopentene-4-methyl amine, cyclopentene-4-ethyl
28 amine, 1-methyl cyclopentene-4-ethyl amine, 3-methyl cyclopentene-4-ethyl
29 amine, 1,2-dimethyl cyclopentene-4-ethyl amine, 3,5-dimethyl cyclopentene-

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- 1 4-ethyl amine, 1,3-dimethyl cyclopentene-4-ethyl amine, 2,3-dimethyl
2 cyclopentene-4-ethyl amine, 1,2,3-trimethyl cyclopentene-4-ethyl amine,
3 1,2,3,5-tetramethyl cyclopentene-4-ethyl amine, cyclopentene-4-propyl
4 amine, 1-methyl cyclopentene-4-propyl amine, 3-methyl cyclopentene-4-
5 propyl amine, 1,2-dimethyl cyclopentene-4-propyl amine, 3,5-dimethyl
6 cyclopentene-4-propyl amine, 1,3-dimethyl cyclopentene-4-propyl amine, 2,3-
7 dimethyl cyclopentene-4-propyl amine, 1,2,3-trimethyl cyclopentene-4-propyl
8 amine, and 1,2,3,5-tetramethyl cyclopentene-4-propyl amine;
- 9 b) heating the polymers and amidizing/transamidizing compounds selected
10 in (a) to form a polymer melt;
- 11 c) processing the melt in an extruder under amidation/transamidation
12 conditions with amidation/transamidation catalysts and antioxidants protecting
13 the melt from oxidation during extrusion, so that the polymer melt undergoes
14 amidation of polymeric anhydrides with cyclic olefin pendent groups,
15 amidation of polymeric acids with cyclic olefin pendent groups or exchange of
16 alkyl groups of polymeric esters with cyclic olefin pendent groups; and
- 17 d) removing volatile organic products and by-products from the melt.
- 18 111. The process of claim 108, wherein the making of the polymer material
19 comprises the steps of:
- 20 (a) adding to an autoclave, ethylene and a vinyl monomer comprising
21 a pendent cyclohexene;
- 22 (b) stirring the ethylene and the vinyl monomer in the autoclave to
23 achieve a mixture;
- 24 (c) adding a polymerization initiator before, during or after the stirring
25 step;
- 26 (d) polymerizing the mixture to achieve a polymer; and
27 (e) isolating and purifying the polymer.

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1

2 112. The process of claim 111, wherein in step (a) an alpha-olefin is added to
3 the autoclave along with the ethylene and the vinyl monomer and in
4 step (b) the alpha-olefin is stirred with the ethylene and the vinyl
5 monomer to achieve the mixture.

6

7 113. The process of claim 109, wherein the polymeric backbone is ethylenic
8 and the linking groups are selected from the group consisting of:

9 $-\text{O}-(\text{CHR})_n-; -(\text{C}=\text{O})-\text{O}-(\text{CHR})_n-; -\text{NH}-(\text{CHR})_n-;$

10 $-\text{O}-(\text{C}=\text{O})-(\text{CHR})_n-; -(\text{C}=\text{O})-\text{NH}-(\text{CHR})_n-;$ and

11 $-(\text{C}=\text{O})-\text{O}-\text{CHOH}-\text{CH}_2-\text{O}-;$

12 where R is hydrogen or an alkyl group selected from the group
13 consisting of methyl, ethyl, propyl and butyl groups and where n is an
14 integer in the range from 1 to 12.

15 114. The process of claim 110, wherein the polymeric backbone is ethylenic
16 backbone and the linking group is:

17 $-(\text{C}=\text{O})-\text{NH}-(\text{CHR})_n$

18 where R is hydrogen or an alkyl group selected from the group
19 consisting of methyl, ethyl, propyl and butyl groups and where n is an
20 integer in the range from 1 to 12.

21 115. The process of claim 108, wherein the material is an oxygen scavenging
22 composition further comprising a transition metal catalyst.

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- 1 116. The process of claim 115, wherein the transition metal catalyst is a
2 metal salt.
3
- 4 117. The process of claim 116, wherein the metal in the metal salt is cobalt.
5
- 6 118. The process according to claim 116, wherein the metal salt is selected
7 from the group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate,
8 cobalt oleate and cobalt stearate.
9
10
- 11 119. The process of claim 115, wherein the oxygen scavenging composition
12 further comprises at least one triggering material to enhance initiation of
13 oxygen scavenging.
14
- 15 120. The process of claim 119, wherein the triggering material is a
16 photoinitiator.
17
18
- 19 121. The process of claim 108, wherein the cyclic olefinic pendent groups
20 have the structure (II):

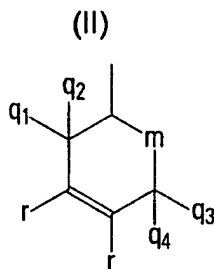
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6 where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$,
 7 $-CH_3$, and $-C_2H_5$; and where m is $-(CH_2)_n-$ and where n is an integer in
 8 the range of from 0 to 4; and wherein when r is $-H$, at least one of q_1 , q_2 ,
 9 q_3 and q_4 is $-H$.

10 122. The process of claim 108, wherein the functional groups with attached
 11 cyclic olefinic pendent groups are grafted onto the linking backbone by a
 12 esterification, transesterification, amidation or transamidation reaction.

13

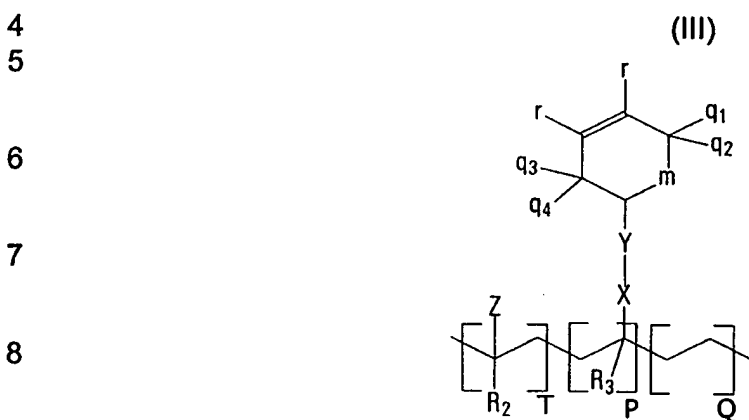
14 123. The process of claim 108, wherein the reaction is a solution reaction or
 15 a reactive extrusion.

16 124. The process of claim 108, wherein the esterification, transesterification,
 17 amidation or transamidation reaction is catalyzed by a catalyst selected from
 18 the group consisting of strong non-oxidizing acids, tertiary amines, Group I
 19 alkoxides, Group IVB alkoxides, Group IVA organometallics.

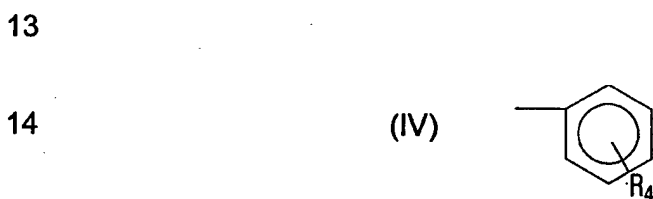
20 125. The process of claim 124, wherein the catalyst is selected from the
 21 group consisting of toluene sulfonic acid, sodium methoxide, tetrabutyl
 22 titanate, tetrakisopropyl titanate, tetra-*n*-propyl-titanate, tetraethyl titanate, 2-
 23 hydroxy-pyridine and dibutyltin dilaurate.

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1 126. The process of claim 108, wherein the backbone, linking groups and
 2 cyclic olefin pendent groups comprise repeating units, each unit having a
 3 structure (III) as follows:



10 wherein P + T + Q is 100 mol % of the total composition; P is greater than 0;
 11 Z is selected from the group consisting of an aryl group, $-(C=O)OR_1$,
 12 $-O(C=O)R_1$ and an alkyl aryl group, structure (IV):



16 where R_4 is selected from the group consisting of $-H$, $-CH_3$ and $-C_2H_5$; R_1 is
 17 selected from the group consisting of $-H$, $-CH_3$, $-C_2H_5$, $-C_3H_5$ and $-C_4H_7$;
 18 R_2 and R_3 is selected from the group consisting of $-H$ and CH_3 ; X is
 19 selected from the group consisting of $O-$, $-NH-$, $-(C=O)O-$, $-(C=O)NH-$,
 20 $-(C=O)S-$, $-O(C=O)-$ and $-(CHR)_\ell-$; ℓ is an integer selected from the
 21 group consisting of 1, 2, 3, 4, 5 and 6; Y is $-(CHR)_n-$, where n is an
 22 integer in the range from 0 to 12 where R is selected from the group

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1 consisting of $-H$, $-CH_3$ and $-C_2H_5$; where q_1 , q_2 , q_3 , q_4 , and r are selected
2 from the group consisting of $-H$, $-CH_3$, and $-C_2H_5$; and where m is
3 $-(CH_2)_n-$ and where n is an integer in the range of from 0 to 4; and
4 wherein when r is $-H$, at least one of q_1 , q_2 , q_3 and q_4 is $-H$.

5 127. The process of claim 108, wherein the cyclic olefinic pendent groups are
6 selected from the group consisting of cyclohexene-4-methylene radical,
7 1-methyl cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-
8 methylene radical, 5-methyl cyclohexene-4-methylene radical,
9 1,2-dimethyl cyclohexene-4-methylene radical, 1,5-dimethyl
10 cyclohexene-4-methylene radical, 2,5-dimethyl cyclohexene-4-
11 methylene radical, 1,2,5-trimethyl cyclohexene-4-methylene radical,
12 cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-ethylene
13 radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl
14 cyclohexene-4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene
15 radical, 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl
16 cyclohexene-4-ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene
17 radical, cyclohexene-4-propylene radical, 1-methyl cyclohexene-4-
18 propylene radical, 2-methyl cyclohexene-4-propylene radical, 5-methyl
19 cyclohexene-4-propylene radical, 1,2-dimethyl cyclohexene-4-propylene
20 radical, 1,5-dimethyl cyclohexene-4-propylene radical, 2,5-dimethyl
21 cyclohexene-4-propylene radical, 1,2,5-trimethyl cyclohexene-4-
22 propylene radical, cyclopentene-4-methylene radical, 1-methyl
23 cyclopentene-4-methylene radical, 3-methyl cyclopentene-4-methylene
24 radical, 1,2-dimethyl cyclopentene-4-methylene radical, 3,5-dimethyl
25 cyclopentene-4-methylene radical, 1,3-dimethyl cyclopentene-4-
26 methylene radical, 2,3-dimethyl cyclopentene-4-methylene radical,
27 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
28 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical,
29 1-methyl cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-

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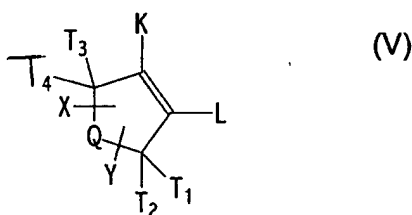
- 1 ethylene radical, 1,2-dimethyl cyclopentene-4-ethylene radical,
2 3,5-dimethyl cyclopentene-4-ethylene radical, 1,3-dimethyl
3 cyclopentene-4-ethylene radical, 2,3-dimethyl cyclopentene-4-ethylene
4 radical, 1,2,3-trimethyl cyclopentene-4-ethylene radical,
5 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-
6 propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl
7 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-
8 propylene radical, 3,5-dimethyl cyclopentene-4-propylene radical,
9 1,3-dimethyl cyclopentene-4-propylene radical, 2,3-dimethyl
10 cyclopentene-4-propylene radical, 1,2,3-trimethyl cyclopentene-4-
11 propylene radical, and 1,2,3,5-tetramethyl cyclopentene-4-propylene
12 radical.
- 13 128. The process of claim 108, wherein the composition is a ethylene/methyl
14 acrylate/cyclohexenyl methyl acrylate terpolymer, a cyclohexenyl methyl
15 acrylate/ethylene copolymer, a cyclohexenyl methyl
16 methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate
17 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate
18 copolymer.

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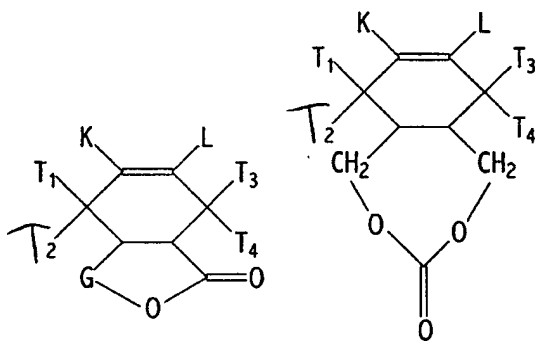
129. A non-odorous oxygen scavenging polymer composition comprising: (1) monomers derived from cyclic hydrocarbon moieties having at least one cyclic allylic or cyclic benzylic hydrogen and (2) a transition metal oxidation catalyst.

130. The composition of claim 129, wherein the composition comprises condensation polymers selected from the group consisting of polyesters, polyamides, polycarbonate, polyurethane, polyureas and polyether.

131. The composition of claim 129, wherein the cyclic allylic monomers are selected from the group consisting of structure (V), structure (VI) and structure (VII):



(V)



(VI)

(VII)

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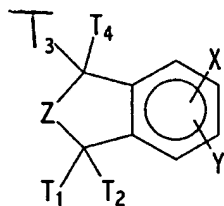
1 with K, L, T₁, T₂, T₃, and T₄ being selected from the group consisting of
 2 -C_qH_{2q+1} with q being an integer in the range from 0 to 12 and wherein,
 3 when either K or L is -H, at least one of T₁, T₂, T₃ and T₄ is -H;
 4 and with X and Y being selected from the group consisting of -(CH₂)_n-
 5 OH, -(CH₂)_n-NH₂, -(CH₂)_nNC=O and -(CH₂)_m-(C=O)-A with n being an
 6 integer in the range from 1 to 12 and m being an integer in the range
 7 from 0 to 12 and A being selected from the group consisting of -OH,
 8 -OCH₃, -OC₂H₅, -OC₃H₇ and halides; and Q being selected from the
 9 group consisting of -(C_tH_{2t-2}) with t being an integer in the range from 1
 10 to 4;
 11 and with G being selected from -(C=O)- and -(C_nH_{2n+1})- with n being an
 12 integer from 0 to 12.

13

14 132. The composition of claim 129, wherein the cyclic benzylic monomers are
 15 selected from the group consisting of structure (VIII), structure (IX), structure
 16 (X), structure (XI), structure (XII), and structure (XIII)

17

18 (VIII)



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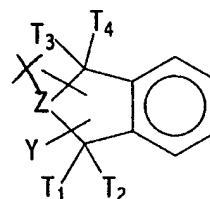
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(IX)



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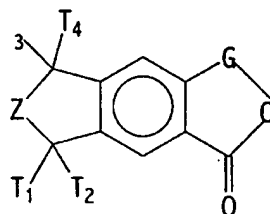
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(X)



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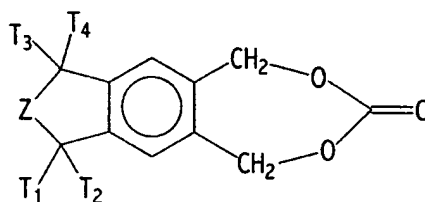
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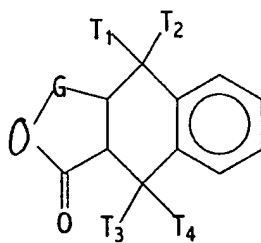
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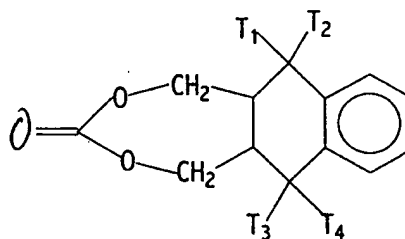
(XI)



(XII)



(XIII)



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- 1 where X and Y are selected from the group consisting of $-(CH_2)_n-OH$,
 2 $-(CH_2)_n-NH_2$ and $-(CH_2)_m-(C=O)-R_1$ with n being an integer in the range
 3 from 1 to 12, and with m being an integer in the range from 0 to 12 and
 4 with R_1 being selected from the group consisting of $-OH$, $-OCH_3$,
 5 $-OC_2H_5$, $-OC_3H_7$ and halides;
 6 with T_1 , T_2 , T_3 , and T_4 being selected from the group consisting of
 7 $-C_qH_{2q+1}$ with q being an integer in the range from 0 to 12 and at least
 8 one of T_1 , T_2 , T_3 and T_4 being $-H$;
 9 and with X and Y being selected from the group consisting of –
 10 $(CH_2)_n-OH$, $-(CH_2)_n-NH_2$, $-(CH_2)_nNC=O$, and $-(CH_2)_m-(C=O)-A$ with n
 11 being an integer in the range from 1 to 12, and m being an integer in the
 12 range from 0 to 12 and A being selected from the group consisting of
 13 $-OH$, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides; and Z being selected from the
 14 group consisting of $-(C_tH_{2t-2})-$, $-O-$, $-NR_2-$, $-S-$, with t being an integer in
 15 the range from 1 to 4 and R_2 being selected from the group consisting of
 16 $-OH$, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides;
 17 and with G being selected from $-(C=O)-$ and $-(C_nH_{2n+1})-$ with n being an
 18 integer from 0 to 12.
- 19
- 20 133. The composition of claim 130, the composition being thermoplastic.
- 21
- 22 134. The composition of claim 130, the composition being thermoset.
- 23
- 24
- 25 135. The composition of claim 130, the composition being a multilayered
 26 structure with other layers being an aromatic polyester or copolyester
 27 selected from the group consisting of polyethylene terephthalate,
 28 polyethylene naphthalate, polypropylene terephthalate, polybutylene
 29 terephthalate, polyethylene isophthalate, polycyclohexanedimethanol

1 terephthalate, polybutylene naphthalate, polycyclohexanedimethanol
2 naphthalate, and copolymers and blends thereof.

3

4 136. The composition of claim 130, the composition being a multilayered
5 structure with other layers being polyamides or copolyamides selected from
6 the group consisting of Nylon 6, Nylon 66, Nylon 610 and mixtures thereof.

7

8

9 137. The composition of claim 130, the composition being a multilayered
10 structure with other layers being bisphenol A carbonate.

11

12 138. The composition of claim 130, the composition being a multilayered
13 structure with other layers being vinylic polymers or copolymers selected
14 from the group consisting of ethylene polymer, ethylene copolymer, propylene
15 polymer, propylene copolymer, styrene polymer, styrene copolymer, acrylate
16 polymer, acrylate copolymer, vinyl chloride polymer, vinyl chloride copolymer,
17 divinyl chloride polymer, divinyl chloride copolymer, fluorinated vinyl polymer,
18 fluorinated vinyl copolymer and mixtures thereof.

19

20

21 139. The composition of claim 130, the composition being blended with an
22 aromatic polyester or copolyester selected from the group consisting of
23 polyethylene terephthalate, polyethylene naphthalate, polypropylene
24 terephthalate, polybutylene terephthalate, polyethylene isophthalate,
25 polycyclohexanedimethanol terephthalate, polybutylene naphthalate,
26 polycyclohexanedimethanol naphthalate, and copolymers and blends thereof.

27

28 140. The composition of claim 130, the composition being blended with
29 polyamides or copolyamides selected from the group consisting of Nylon 6,
30 Nylon 66, Nylon 610 and mixtures thereof.

1 141. The composition of claim 130, the composition being blended with
2 bisphenol A polycarbonate.

3

4 142. The composition of claim 130, the composition being a blend comprising
5 vinylic polymers or copolymers selected from the group consisting of ethylene
6 polymer, ethylene copolymer, propylene polymer, propylene copolymer,
7 styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer,
8 vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer,
9 divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl
10 copolymer and mixtures thereof.

11

12

13 143. The composition of claim 130, the composition being laminated or
14 adhering onto a substrate selected from the group consisting of paper, foil,
15 high temperature film, metallized film, polyamide films, ethylene vinyl alcohol
16 film, silica coated film, nylon/EVOH/nylon, oriented polypropylene, polyester
17 film, polyethylene, polypropylene, polyester, oriented polyethylene
18 terephthalate and cellophane.

19

20 144. The composition of claim 129, wherein the composition comprises a
21 vinyl polymer selected from the group consisting of ethylene polymer,
22 ethylene copolymer, propylene polymer, propylene copolymer, styrene
23 polymer, styrene copolymer and mixtures thereof.

24

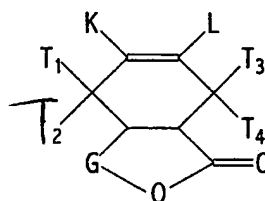
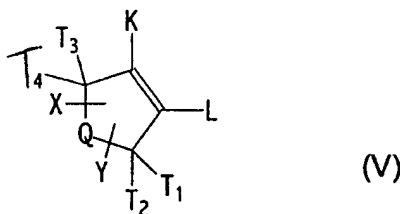
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26 145. A rigid container for food or beverage, the container being molded from
27 a resin comprising a non-odorous oxygen scavenging polymer composition,
28 the composition comprising (1) monomers derived from cyclic hydrocarbon
29 moieties having at least one cyclic allylic or cyclic benzylic hydrogen and (2) a
30 transition metal oxidation catalyst.

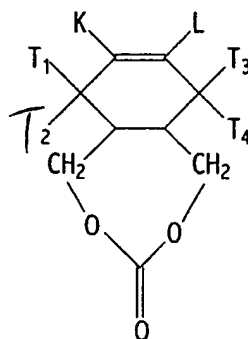
-153-

1 146. The rigid container of claim 145, wherein the composition comprises
2 condensation polymers selected from the group consisting of polyesters,
3 polyamides, polycarbonate, polyurethane, polyureas, polysulfones and
4 polyether.

5
6 147. The rigid container of claim 145, wherein the cyclic allylic monomers are
7 selected from the group consisting of structure (V), structure (VI) and
8 structure (VII):
9



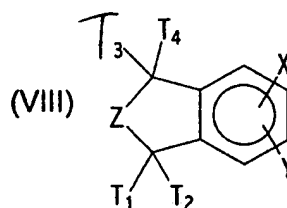
-154-

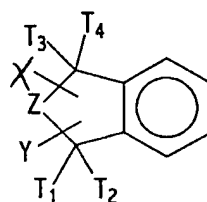


(VII)

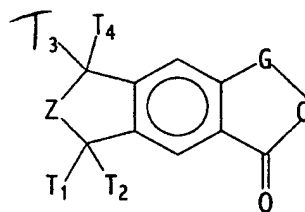
with K, L, T₁, T₂, T₃, and T₄ being selected from the group consisting of -C_qH_{2q+1} with q being an integer in the range from 0 to 12 and wherein, when either K or L is -H, at least one of T₁, T₂, T₃ and T₄ is -H; and with X and Y being selected from the group consisting of -(CH₂)_n-OH, -(CH₂)_n-NH₂, -(CH₂)_nNC=O and -(CH₂)_m-(C=O)-A with n being an integer in the range from 1 to 12 and m being an integer in the range from 0 to 12 and A being selected from the group consisting of -OH, -OCH₃, -OC₂H₅, -OC₃H₇ and halides; and Q being selected from the group consisting of -(C_tH_{2t-2}) with t being an integer in the range from 1 to 4; and with G being selected from -(C=O)- and -(C_nH_{2n+1})- with n being an integer from 0 to 12.

148. The rigid container of claim 145, wherein the cyclic benzylic monomers are selected from the group consisting of structure (VIII), structure (IX), structure (X), structure (XI), structure (XII), and structure (XIII)

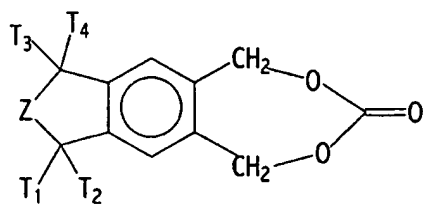




(IX)

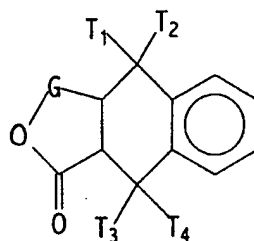


(X)

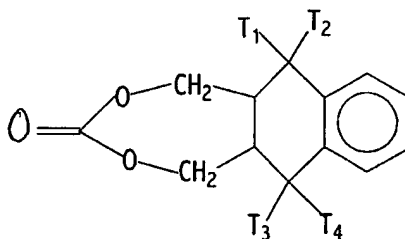


(XI)

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(XII)



(XIII)

where X and Y are selected from the group consisting of $-(CH_2)_n-OH$, $-(CH_2)_n-NH_2$ and $-(CH_2)_m-(C=O)-R_1$ with n being an integer in the range from 1 to 12 and with m being an integer in the range from 0 to 12 and with R_1 being selected from the group consisting of $-OH$, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides;

with T_1 , T_2 , T_3 , and T_4 being selected from the group consisting of $-C_qH_{2q+1}$ with q being an integer in the range from 0 to 12 and at least one of T_1 , T_2 , T_3 and T_4 being $-H$;

and with X and Y being selected from the group consisting of $-(CH_2)_n-OH$, $-(CH_2)_n-NH_2$, $-(CH_2)_nNC=O$ and $-(CH_2)_m-(C=O)-A$ with n being an integer in the range from 1 to 12 and m being an integer in the range from 0 to 12 and A being selected from the group consisting of $-OH$, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides; and Z being selected from the group consisting of $-(C_tH_{2t+2})-$, $-O-$, $-NR_2-$, $-S-$, with t being an integer in

-157-

1 the range from 1 to 4 and R_2 being selected from the group consisting of
2 $-\text{OH}$, $-\text{OCH}_3$, $-\text{OC}_2\text{H}_5$, $-\text{OC}_3\text{H}_7$ and halides;
3 and with G being selected from $-(\text{C}=\text{O})-$ and $-(\text{C}_n\text{H}_{2n+1})-$ with n being an
4 integer from 0 to 12.

5

6 149. The rigid container of claim 146, the composition being thermoplastic.

7 150. The rigid container of claim 146, the composition being thermoset.

8

9

10 151. The rigid container of claim 146, the composition being made by
11 coextrusion, blow molding or lamination with an aromatic polyester or
12 copolyester selected from the group consisting of polyethylene terephthalate,
13 polyethylene naphthalate, polypropylene terephthalate, polybutylene
14 terephthalate, polyethylene isophthalate, polycyclohexanedimethanol
15 terephthalate, polybutylene naphthalate, polycyclohexanedimethanol
16 naphthalate, and copolymers and blends thereof.

17

18 152. The rigid container of claim 146, the composition being made by
19 coextrusion, blow molding or lamination with polyamides or copolyamides
20 selected from the group consisting of Nylon 6, Nylon 66, Nylon 610 and
21 mixtures thereof.

22

23

24 153. The rigid container of claim 146, the composition being made by
25 coextrusion, blow molding or lamination with bisphenol A polycarbonate.

26

27 154. The rigid container of claim 146, the composition being made by
28 coextrusion, blow molding or lamination with vinylic polymers or copolymers
29 selected from the group consisting of ethylene polymer, ethylene copolymer,
30 propylene polymer, propylene copolymer, styrene polymer, styrene

1 copolymer, acrylate polymer, acrylate copolymer, vinyl chloride polymer, vinyl
2 chloride copolymer, divinyl chloride polymer, divinyl chloride copolymer,
3 fluorinated vinyl polymer, fluorinated vinyl copolymer and mixtures thereof.

4
5
6 155. The rigid container of claim 146, the composition being blended with
7 an aromatic polyester or copolyester selected from the group consisting of
8 polyethylene terephthalate, polyethylene naphthalate, polypropylene
9 terephthalate, polybutylene terephthalate, polyethylene isophthalate,
10 polycyclohexanedimethanol terephthalate, polybutylene naphthalate,
11 polycyclohexanedimethanol naphthalate, and copolymers and blends thereof.

12
13 156. The rigid container of claim 146, the composition being blended with
14 polyamides or copolyamides selected from the group consisting of Nylon 6,
15 Nylon 66, Nylon 610 and mixtures thereof.

16
17
18 157. The rigid container of claim 146, the composition being blended with
19 bisphenol A carbonate.

20
21 158. The rigid container of claim 146, the composition being blended with
22 vinylic polymers or copolymers selected from the group consisting of ethylene
23 polymer, ethylene copolymer, propylene polymer, propylene copolymer,
24 styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer,
25 vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer,
26 divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl
27 copolymer and mixtures thereof.

28

29

1 159. The rigid container of claim 146, the composition being laminated or
2 adhering onto a substrate selected from the group consisting of paper, foil,
3 high temperature film, metallized film, polyamide films, ethylene vinyl alcohol
4 film, silica coated film, nylon/EVOH/nylon, oriented polypropylene, polyester
5 film, oriented polyethylene terephthalate, polypropylene, polyester, and
6 cellophane.

7 160. The rigid container of claim 146, wherein the composition comprises
8 a vinyl polymer selected from the group consisting of ethylene polymer,
9 ethylene copolymer, propylene polymer, propylene copolymer, styrene
10 polymer, styrene copolymer and mixtures thereof.

11

12 161. The rigid container according to claim 145, wherein the composition is
13 a single layer.

14

15

16 162. The rigid container according to claim 145, wherein the composition is
17 multilayered.

18

19 163. The rigid container according to claim 162, wherein the composition
20 comprises an outer air contact layer and an inner oxygen scavenging layer.

21

22

23 164. The rigid container according to claim 163, wherein the outer air
24 contact layer comprises an oxygen barrier resin selected from the group
25 consisting of polyethylene terephthalate, polyethylene naphthalate and a
26 mixture of polyethylene terephthalate and polyethylene naphthalate.

27

28 165. The rigid container according to claim 163, wherein the composition
29 further comprises at least one of an inner food contact layer, a tie layer, and a
30 tinted ultraviolet protection layer.

1

2

3 166. The rigid container according to claim 165, wherein the inner food
4 contact layer comprises an oxygen barrier resin selected from the group
5 consisting of polyethylene terephthalate, polyethylene naphthalate and a
6 mixture of polyethylene terephthalate and polyethylene naphthalate.

7

8 167. The rigid container of claim 145, wherein oxygen scavenging by the
9 non-odorous oxygen scavenging polymer composition is initiated by moisture
10 or actinic radiation.

11

12

13 168. The rigid container of claim 145, wherein the transition metal catalyst
14 is a metal salt.

15

16 169. The rigid container of claim 168, wherein the metal in the metal salt is
17 cobalt.

18

19

20 170. The rigid container of claim 169, wherein the metal salt is selected
21 from the group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate,
22 cobalt oleate and cobalt stearate.

23

24 171. The rigid container of claim 145, wherein the non-odorous oxygen
25 scavenging composition further comprises at least one triggering material to
26 enhance initiation of oxygen scavenging.

27

28

29 172. The rigid container of claim 171, wherein the triggering material is a
30 photoinitiator.

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1

2 173. The rigid container of claim 172, wherein the photoinitiator has an
3 ultraviolet absorption window above 320 nm.

4 174. The rigid container of claim 172, wherein the container further comprises
5 a tinted ultraviolet protection layer located between the layer comprising the
6 non-odorous oxygen scavenging composition and the inside of the rigid
7 container.

8

9 175. The rigid container of claim 174, wherein the tinted layer is the food
10 contact layer.

11

12

13 176. The rigid container of claim 174, wherein the resin comprises
14 condensation polymers selected from the group consisting of polyesters,
15 polyamides, polyurethane, polyureas, polysulfones, polycarbonates and
16 polyether.

17

18 177. The rigid container of claim 174, wherein the cyclic allylic monomers
19 are selected from the group consisting of structure (V), structure (VI) and
20 structure (VII):

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22

23

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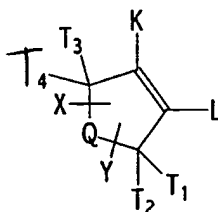
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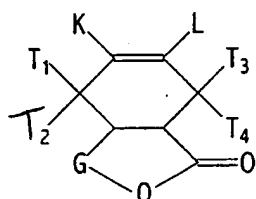
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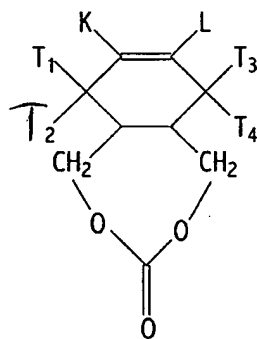


(V)

-162-



(VI)



(VII)

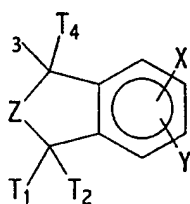
with K, L, T₁, T₂, T₃, and T₄ being selected from the group consisting of
 $-C_qH_{2q+1}$ with q being an integer in the range from 0 to 12 and wherein,
 when either K or L is -H, at least one of T₁, T₂, T₃ and T₄ is -H;
 and with X and Y being selected from the group consisting of
 $-(CH_2)_n-OH$, $-(CH_2)_n-NH_2$, $-(CH_2)_nNC=O$ and $-(CH_2)_m-(C=O)-A$ with n being
 an integer in the range from 1 to 12 and m being an integer in the range

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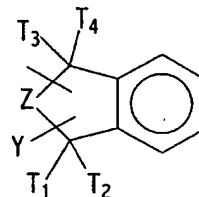
from 0 to 12 and A being selected from the group consisting of -OH, -OCH₃, -OC₂H₅, -OC₃H₇ and halides; and Q being selected from the group consisting of -(C_tH_{2t-2}) with t being an integer in the range from 1 to 4; and with G being selected from -(C=O)- and -(C_nH_{2n+1})- with n being an integer from 0 to 12.

178. The rigid container of claim 174, wherein the cyclic benzylic monomers are selected from the group consisting of structure (VIII), structure (IX), structure (X), structure (XI), structure (XII), and structure (XIII):

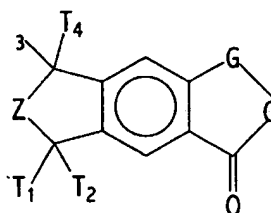
(VIII)



(IX)

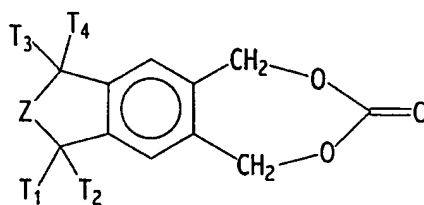


(X)



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(XI)

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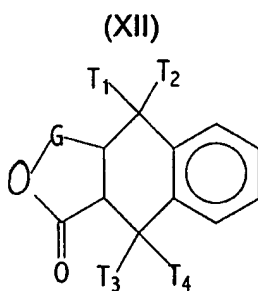
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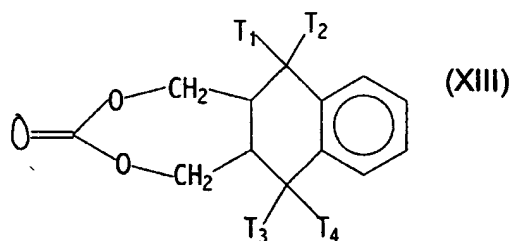
21

22

23



(XII)



(XIII)

24 where X and Y are selected from the group consisting of $-(CH_2)_n-OH$,
 25 $-(CH_2)_n-NH_2$ and $-(CH_2)_m-(C=O)-R_1$ with n being an integer in the range
 26 from 1 to 12 and with m being an integer in the range from 0 to 12 and

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1 with R_1 being selected from the group consisting of -OH, -OCH₃, -OC₂H₅,
2 -OC₃H₇ and halides;
3 with T_1 , T_2 , T_3 , and T_4 being selected from the group consisting of
4 -C_qH_{2q+1} with q being an integer in the range from 0 to 12 and at least
5 one of T_1 , T_2 , T_3 and T_4 being -H;
6 and with X and Y being selected from the group consisting of
7 -(CH₂)_n-OH, -(CH₂)_n-NH₂, -(CH₂)_nNC=O and -(CH₂)_m-(C=O)-A with n
8 being an integer in the range from 1 to 12 and m being an integer in the
9 range from 0 to 12 and A being selected from the group consisting of
10 -OH, -OCH₃, -OC₂H₅, -OC₃H₇ and halides; and Z being selected from the
11 group consisting of -(C_tH_{2t-2})-, -O-, -NR₂-, -S-, with t being an integer in
12 the range from 1 to 4 and R₂ being selected from the group consisting of
13 -OH, -OCH₃, -OC₂H₅, -OC₃H₇ and halides;
14 and with G being selected from -(C=O)- and -(C_nH_{2n+1})- with n being an
15 integer from 0 to 12.

16

17 179. The rigid container of claim 176, the composition being thermoplastic.

18

19 180. The rigid container of claim 176, the composition being thermoset.

20

21

22 181. The rigid container of claim 176, the composition being in a multilayer
23 structure with other layers, at least one of the other layers comprising an
24 aromatic polyester or copolyester selected from the group consisting of
25 polyethylene terephthalate, polyethylene naphthalate, polypropylene
26 terephthalate, polybutylene terephthalate, polyethylene isophthalate,
27 polycyclohexanedimethanol terephthalate, polybutylene naphthalate,
28 polycyclohexanedimethanol naphthalate, and copolymers and blends
29 thereof.

30

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1 182. The rigid container of claim 176, the composition being in a multilayer
2 structure with other layers, at least one of the other layers comprising
3 polyamides or copolyamides selected from the group consisting of Nylon 6,
4 Nylon 66, Nylon 610 and mixtures thereof.

5

6 183. The rigid container of claim 176, the composition being in a multilayer
7 structure with other layers, at least one of the other layers comprising
8 bisphenol A carbonate.

9

10

11 184. The rigid container of claim 176, the composition being in a multilayer
12 structure with other layers, at least one of the other layers comprising vinylic
13 polymers or copolymers selected from the group consisting of ethylene
14 polymer, ethylene copolymer, propylene polymer, propylene copolymer,
15 styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer,
16 vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer,
17 divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl
18 copolymer and mixtures thereof.

19

20 185. The rigid container of claim 176, the composition being blended with an
21 aromatic polyester or copolyester selected from the group consisting of
22 polyethylene terephthalate, polyethylene naphthalate, polypropylene
23 terephthalate, polybutylene terephthalate, polyethylene isophthalate,
24 polycyclohexanedimethanol terephthalate, polybutylene naphthalate,
25 polycyclohexanedimethanol naphthalate, and copolymers and blends thereof.

26

27

28 186. The rigid container of claim 176, the composition being blended with
29 polyamides or copolyamides selected from the group consisting of Nylon 6,
30 Nylon 66, Nylon 610 and mixtures thereof.

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1

2 187. The rigid container of claim 176, the composition being blended with
3 bisphenol A carbonate.

4

5

6 188. The rigid container of claim 176, the composition being blended with
7 vinylic polymers or copolymers selected from the group consisting of ethylene
8 polymer, ethylene copolymer, propylene polymer, propylene copolymer,
9 styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer,
10 vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer,
11 divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl
12 copolymer and mixtures thereof.

13

14 189. The rigid container of claim 176, the composition being laminated or
15 adhering onto a substrate selected from the group consisting of paper, foil,
16 high temperature film, metallized film, polyamide films, ethylene vinyl alcohol
17 film, silica coated film, nylon/EVOH/nylon, oriented polypropylene, polyester
18 film, polyethylene, polypropylene, oriented polyethylene terephthalate, and
19 cellophane.

20

21

22 190. The rigid container of claim 176, wherein the composition comprises a
23 vinyl polymer selected from the group consisting of ethylene polymer,
24 ethylene copolymer, propylene polymer, propylene copolymer, styrene
25 polymer, styrene copolymer and mixtures thereof.

26 191. The rigid container according to claim 176, wherein the composition
27 comprises an outer air contact layer and an inner oxygen scavenging layer.

28

29 192. The rigid container according to claim 191, wherein the outer air contact
30 layer comprises an oxygen barrier resin selected from the group consisting of

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1 polyethylene terephthalate, polyethylene naphthalate and a mixture of
2 polyethylene terephthalate and polyethylene naphthalate.

3

4

5 193. The rigid container according to claim 176, wherein the composition
6 further comprises at least one of an inner food contact layer, a tie layer, and a
7 tinted ultraviolet protection layer.

8

9 194. The rigid container according to claim 193, wherein the inner food
10 contact layer comprises an oxygen barrier resin selected from the group
11 consisting of polyethylene terephthalate, polyethylene naphthalate and a
12 mixture of polyethylene terephthalate and polyethylene naphthalate.

13

14

15 195. The rigid container of claim 176, wherein the transition metal catalyst is
16 a metal salt.

17

18 196. The rigid container of claim 195, wherein the metal in the metal salt is
19 cobalt.

20

21

22 197. The rigid container of claim 196, wherein the metal salt is selected from
23 the group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate, cobalt
24 oleate and cobalt stearate.

25 198. The rigid container of claim 197, wherein the triggering material is a
26 photoinitiator.

27

28 199. The rigid container of claim 198, wherein the photoinitiator has an
29 ultraviolet absorption window above 320 nm.

30

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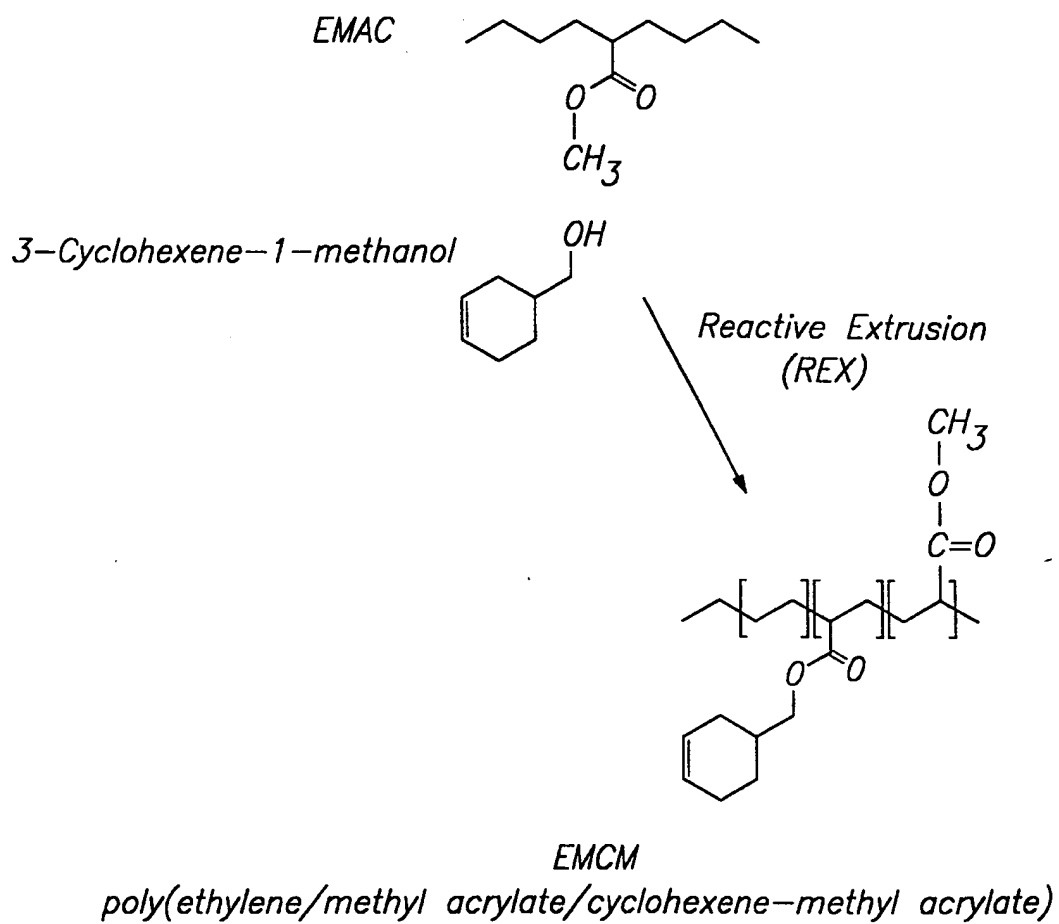
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2 200. The rigid container of claim 145, wherein the rigid container is suitable
3 for packaging oxygen sensitive drinks for extended freshness and shelf life.

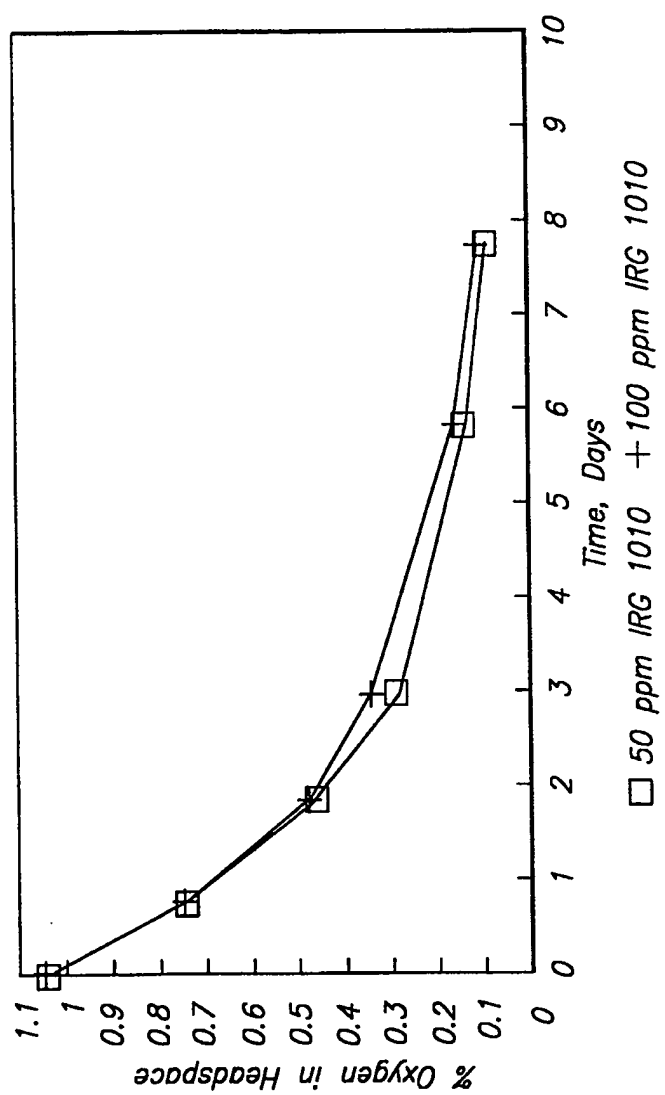
4

5 201. The rigid container of claim 200, wherein the oxygen sensitive drink is
6 beer.

1/5

**FIG. 1**

2/5

**FIG. 2**

3/5

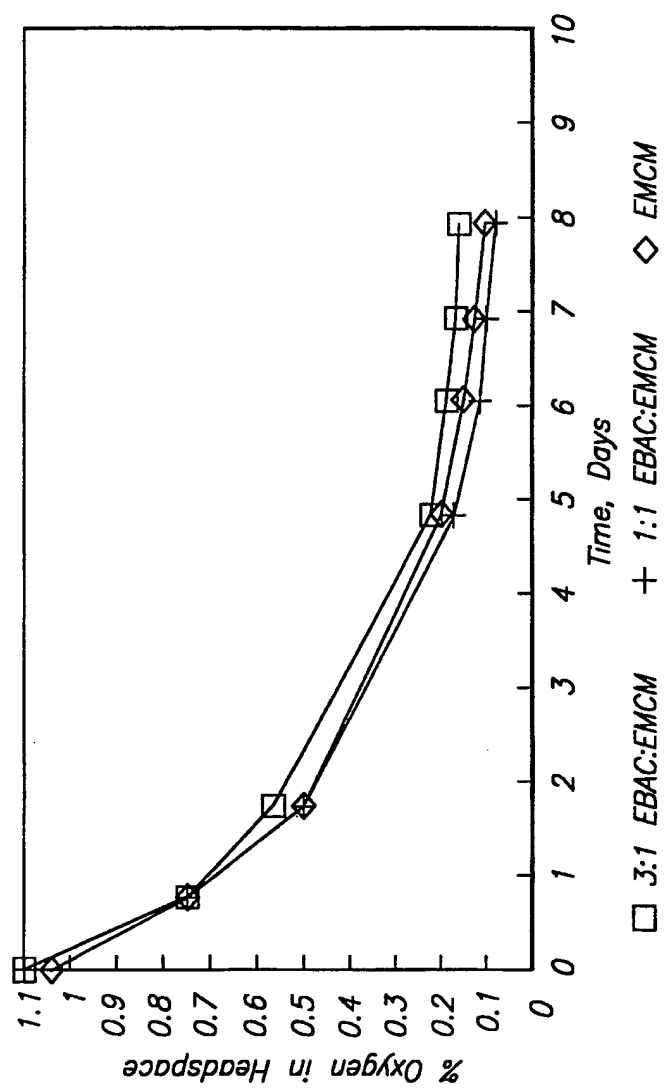


FIG. 3

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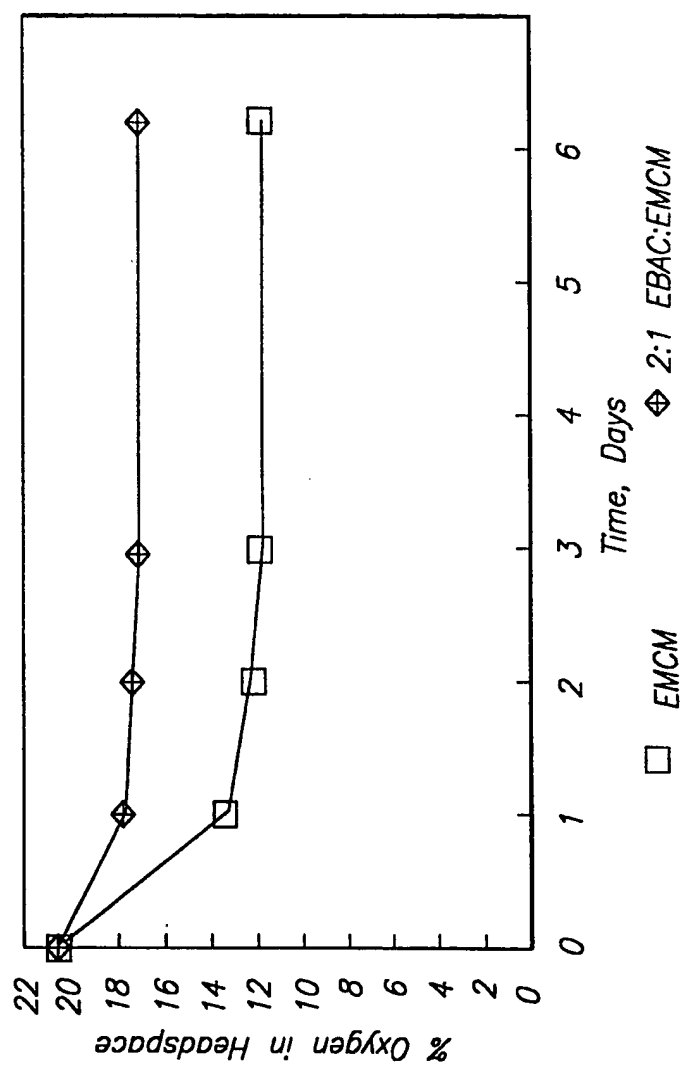
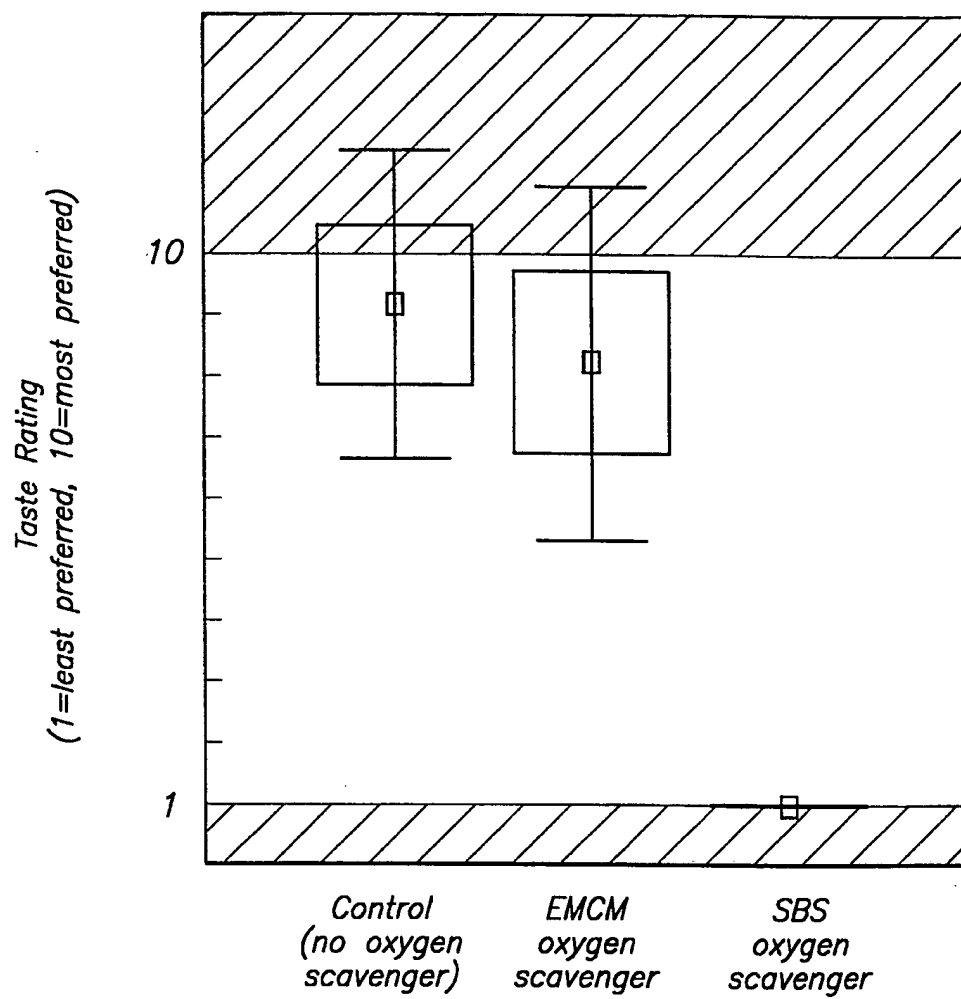


FIG. 4

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**FIG. 5**



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| | | | |
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| (22) International Filing Date: 24 March 1999 (24.03.99) | | | |
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| (71) Applicants: CHEVRON CHEMICAL COMPANY LLC [US/US]; 555 Market Street, San Francisco, CA 94105 (US). SEALED AIR (NZ) LIMITED [NZ/NZ]; Private Bag 3085, Corner Avalon Drive & Foreman Road (NZ). | | | |
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| | | (88) Date of publication of the international search report: 11 November 1999 (11.11.99) | |
| (54) Title: OXYGEN SCAVENGERS WITH REDUCED OXIDATION PRODUCTS FOR USE IN PLASTIC FILMS AND BEVERAGE AND FOOD CONTAINERS | | | |
| <p style="text-align: center;">EMAC</p> <p style="text-align: center;">3-Cyclohexene-1-methanol</p> <p style="text-align: center;">Reactive Extrusion (REX)</p> <p style="text-align: center;">EMCM</p> <p style="text-align: center;"><i>poly(ethylene/methyl acrylate/cyclohexene-methyl acrylate)</i></p> | | | |
| (57) Abstract | | | |
| <p>An oxygen scavenger composition, for use in or with plastics materials, includes a polymer or oligomer having at least one cyclohexene group or functionality. The composition produces only low levels of volatile or (extractable from a plastics material in which it is incorporated) products as a consequence of oxygen scavenging. A family of polymers containing selected cyclic allylic pendent groups for oxygen scavenging packaging which has minimal organoleptic by-products after oxidation. Multilayer plastic containers for food and beverage packaging which incorporate oxygen scavenging resins which selectively oxidize upon activation without giving off odorous fragments.</p> | | | |

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| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | | Republic of Macedonia | TR | Turkey |
| BG | Bulgaria | HU | Hungary | ML | Mali | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MN | Mongolia | UA | Ukraine |
| BR | Brazil | IL | Israel | MR | Mauritania | UG | Uganda |
| BY | Belarus | IS | Iceland | MW | Malawi | US | United States of America |
| CA | Canada | IT | Italy | MX | Mexico | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NE | Niger | VN | Viet Nam |
| CG | Congo | KE | Kenya | NL | Netherlands | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NO | Norway | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's | NZ | New Zealand | | |
| CM | Cameroon | | Republic of Korea | PL | Poland | | |
| CN | China | KR | Republic of Korea | PT | Portugal | | |
| CU | Cuba | KZ | Kazakstan | RO | Romania | | |
| CZ | Czech Republic | LC | Saint Lucia | RU | Russian Federation | | |
| DE | Germany | LI | Liechtenstein | SD | Sudan | | |
| DK | Denmark | LK | Sri Lanka | SE | Sweden | | |
| EE | Estonia | LR | Liberia | SG | Singapore | | |

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/06379

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/09

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | WO 96 40799 A (CHEVRON CHEM CO) 19 December 1996 (1996-12-19) cited in the application page 30, line 14 - page 31, line 22; claims 1,3; example 44; tables 4,7-9 --- | 1-30 |
| X | EP 0 040 983 A (UNIV CALIFORNIA) 2 December 1981 (1981-12-02) page 14, line 10-15; claims 1,3,7,8 --- | 1,5 |
| X | DE 19 00 181 A (DEUTSCHE AKADEMIE DER WISSENSCHAFTEN BERLIN) 2 October 1969 (1969-10-02) page 3, line 20-30; example 1 --- | 1,5 |
| X | EP 0 418 011 A (SERICOL GROUP LTD) 20 March 1991 (1991-03-20) claims 1-6; example 1 --- | 1,5 |
| -/- | | |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

15 June 1999

Date of mailing of the international search report

24. 09. 99

Name and mailing address of the ISA

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Devriese, K

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/06379

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | <p>WO 95 02616 A (CHEVRON RES & TECH) 26 January 1995 (1995-01-26) cited in the application -----</p> | 1 |

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/06379

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 - 30

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 99/06379

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-30

a composition comprising: a) a polymer or oligomer with cyclohexene functionality and b) a transition metal catalyst;

2. Claims: 30-107

a polymer with cyclic olefinic pendant groups, a composition and article thereof

3. Claims: 31-41, 108-128

a polymer with cyclic olefinic pendant groups, a process for its manufacture

4. Claims: 129-201

a composition containing a) a polymer b) monomers having a cyclic allylic hydrogen and c) a transition metal catalyst; a container moulded from said composition.

5. Claims: 129-201

a composition containing a) a polymer b) monomers having a cyclic benzylic hydrogen and c) a transition metal catalyst; a container moulded from said composition.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/06379

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|--|--|
| WO 9640799 A | 19-12-1996 | AU 5632696 A BR 9609232 A CA 2218381 A EP 0830386 A | 30-12-1996 11-05-1999 19-12-1996 25-03-1998 |
| EP 0040983 A | 02-12-1981 | JP 57011801 A | 21-01-1982 |
| DE 1900181 A | 02-10-1969 | CS 151502 B | 19-10-1973 |
| EP 0418011 A | 20-03-1991 | GB 2235925 A AT 163298 T AU 6105790 A DE 69032055 D JP 3238456 A | 20-03-1991 15-03-1998 21-03-1991 26-03-1998 24-10-1991 |
| WO 9502616 A | 26-01-1995 | AU 696208 B AU 3750797 A AU 684810 B AU 7361094 A CA 2144309 A DE 69410962 D DE 69410962 T EP 0659195 A JP 8505183 T NO 950926 A NZ 269918 A US 5736616 A US 5627239 A US 5859145 A | 03-09-1998 20-11-1997 08-01-1998 13-02-1995 26-01-1995 16-07-1998 08-10-1998 28-06-1995 04-06-1996 04-05-1995 27-08-1996 07-04-1998 06-05-1997 12-01-1999 |